Pearson Edexcel IAL CHEMISTRY

WCH14/WCH15

REVISION GUIDE

How fast? - rates

1 TERMINOLOGY

Rate of reaction: The rate with which the concentration of a product increases or the rate with which the concentration of a reactant decreases.

Rate equation: An expression relating the rate of a reaction to the concentrations of the reactants present in the reaction mixture.

Order of reaction: The way in which the rate of reaction varies with the concentrations of the reacting substances.

Rate constant: The proportionality constant between the rate of reaction and the products of concentrations that determine how the rate varies with concentration.

Half-life: The time taken for the concentration of a reactant to decrease to half its original value.

Rate-determining step: The slowest step in a chemical reaction.

Activation energy: The minimum energy required to start a reaction by breaking bonds.

Heterogeneous catalyst: A catalyst in a different phase from the reactants.

Homogeneous catalyst: A catalyst in the same phase as the reactants.

2 THE RATE OF REACTION

$$rate = \frac{d[product]}{dt} = -\frac{d[reactant]}{dt}$$

[]→ "concentration"

Rate is measured in units of concentration per unit time, and the most common unit is mol dm^{-3}. The negative sign in the second expression reflects the fact that the concentration of the reactant is decreasing and therefore gives a positive value for the rate.

3 METHODS OF MEASURING THE RATE OF REACTION

Any methods used to find out rates of reactions must employ a technique which measures either the decreasing concentration of reactants or the increasing concentration of products with respect to time.

Production of a gas: Either measure the volume produced at different times collected over water or in a gas syringe or the time to produce a fixed volume of gas. This is a suitable method for most of the gas-producing reactions, such as the decomposition of hydrogen peroxide.

→ Clock reactions: In a clock reaction, the reactants are mixed and the time taken to produce a fixed amount of product is measured. This gives the initial rate of the reaction.

Production of a solid: The time taken to produce enough solid to hide a cross on a piece of paper under the reaction apparatus or on the side of the apparatus can be measured. This method is used to measure the decomposition of sodium thiosulfate by acid.

Loss of mass: Measure the mass of the total reaction mixture as the reaction progresses, and see how quickly it decreases. This is suitable when considering the rate of reaction between calcium carbonate and hydrochloric acid, because as carbon dioxide escapes, mass decreases.

Colour change: The change in colour of either a reactant or a product is measured using a colorimeter. A reaction that can be studied in this way is the reaction between iodine and propanone. The decrease in the intensity of the colour of iodine can be measured with a colorimeter as a function of time.

Conductivity: It involves measuring the conductivity changes in a reaction mixture over time. These reflect the changes in the ions present in the solution.

Titrimetric analysis: This involves removing small portions (aliquots) of the reaction mixture at regular intervals. These aliquots are usually added to another reagent, which immediately stops or quenches the reaction. There are no further changes to the concentrations in the reacting mixture. The quenched aliquots are then titrated to find the concentrations of known compounds in them.

Conductimetric analysis: The number and type of ions in a solution affect its electrical conductivity. As some chemical reactions take place in solution, the ionic balance changes and the resulting change in conductivity can be used to measure the rate of the reaction. These reflect the changes in the ions present in the solution and so can be used to measure the changes in concentration of the various components of the mixture.

4 RATE EQUATIONS, RATE CONSTANTS AND THE ORDER OF A REACTION

A rate equation shows how changes in the concentration of reactants affect the rate of a reaction.

$$A + B \rightarrow \text{products}$$

The equation that describes how the rate varies with the concentrations of the reactants takes this form:

$$\text{rate} = k[A]^m[B]^n \text{ , where k is the rate constant.}$$

The values m and n represent the reaction orders and often are whole numbers or equal to zero. Fractions are uncommon.

$$\text{Overall order of the reaction} = m + n$$

- Every reaction has its own particular rate equation and its own rate constant.
- Rate constants will only change their value with a change in temperature.

The order of a reaction describes the way in which the rate of reaction varies with the concentrations of the reacting substances. The usual relationship is that the rate of reaction is directly proportional to the concentration. However, in some cases the rate of reaction might be directly proportional to the square of the concentration or the rate may not increase at all for increasing concentrations.

Rate equations for different orders of reaction

- Zero order rate equation: rate = $k[A]^0$ or rate = k
- First order rate equation: rate = k[A]
- Second order rate equation: rate = $k[A]^2$

If two or more reactants are involved, then it is possible to have a third order rate equation:

- Third order rate equation: rate = $k[A]^2[B]$

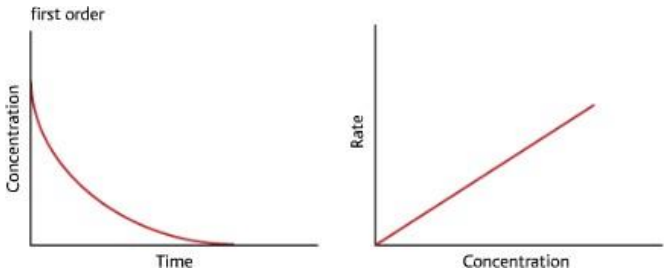
Units of the rate constant

The units of the rate constant differ for different reaction orders. These units can be worked out from the rate equations.

Order	Unit
Zero	mol dm^{-3} s^{-1}
First	s^{-1}
Second	dm^3 mol^{-1} s^{-1}
Third	dm^6 mol^{-2} s^{-1}

1. First order reactions

A reaction is first order with respect to a reactant if the rate of reaction is proportional to the concentration of that reactant. This means that doubling the concentration of the reactant leads to a doubling of the rate of reaction. Hence, a plot of rate against concentration gives a straight line passing through the origin, whereas a graph of concentration of a reactant and time is a decreasing exponential graph as shown:

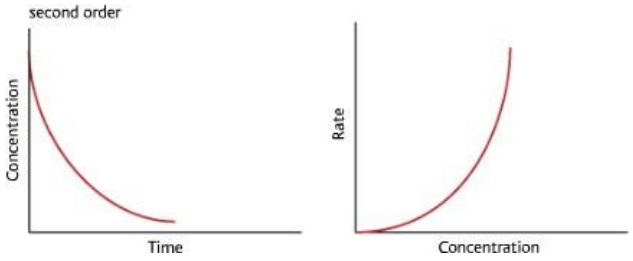


Half-life of a first order reaction

Half-life is independent of concentration and all first order reactions have constant half-lives at a given temperature. The time taken for the concentration to halve is known as the half-life ($t_{1/2}$) of the reaction. If the half-live is short, the reaction is rapid; if the half-life is long the reaction is slow.

2. Second order reactions

A reaction is second order with respect to a reactant if the rate of reaction is proportional to the concentration of that reactant squared. This means that doubling the concentration of a reactant increases the rate by a factor of four.



- A graph of rate against concentration squared for a second order reaction would be a straight line through the origin.

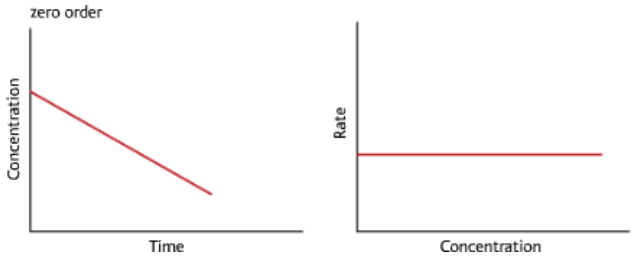
Half-life of a second order reaction

The half-life of a first order reaction is independent of the initial concentration of the reactants. However, the half-life of a second order reaction does depend on the initial concentrations of the reactants. **In second order reactions, halving the initial concentration doubles the half-life.** In other words, in second order reactions the half-life is inversely proportional to the initial concentration of the reactants. It is related to the rate constant by the following equation:

$$t_{1/2} = \frac{1}{k \times [reactant]_{initial}}$$

3. Zero order reactions

A reaction is zero order with respect to a reactant if the rate of reaction is unaffected by changes in the concentration of that reactant.



In summary,

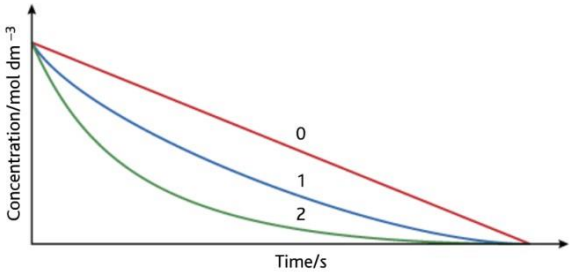


fig. 1.1.18 Graphs of zero, first and second order reactions showing how concentration changes with time.

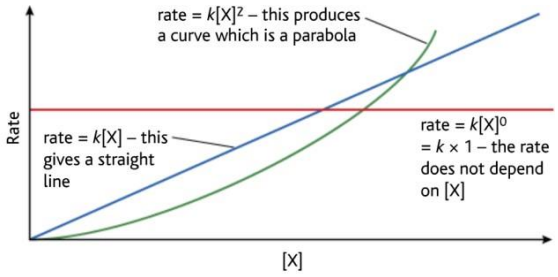

rate = k[X]² – this produces a curve which is a parabola
Rate
rate = k[X] – this gives a straight line
rate = k[X]⁰ = k × 1 – the rate does not depend on [X]
[X]

fig. 1.1.19 The variation of reaction rate with [X] for reactions which are zero, first and second order with respect to X.

5 Determining the order of a reaction and the rate equation from experimental data

It is not possible to predict the order of reaction from a balanced equation. **It has to be found out by experiment**.

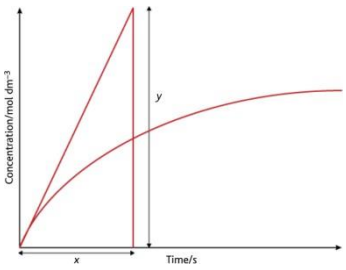
Interpreting experimental data

Once the changes in concentration have been measured in an experiment, the reaction rate can be obtained by plotting concentration against time.

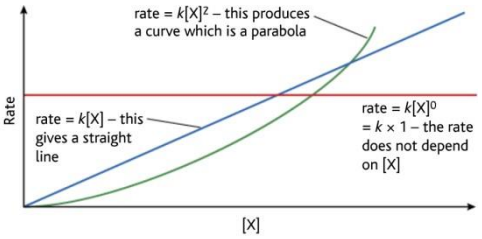
The graph is steepest at the start of a reaction, and it gradually gets less steep as the reaction processes. If such a graph becomes horizontal then the reaction has finished. The rate of reaction decreases with time because the number of particles of A and B decrease and so there are fewer collisions.

To find the rate of a reaction at a particular time, a tangent has to be drawn to the curve at that time and its gradient calculated.

6 Order of reaction from initial rate of reaction



A series of experiments is carried out using different initial concentrations of the reagent under consideration, with every other factor kept constant. It is important that only one variable is changed. For each experiment and product, a concentration against time graph is plotted and a **tangent is drawn to the curve at t=0**. Using a large triangle for maximum accuracy, the gradient is calculated. This is the initial rate of the reaction. **The shape of the graph indicates the order of the reaction with respect to [X] as shown**.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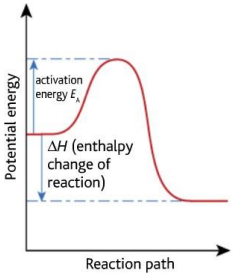
7 ACTIVATION ENERGY AND TYPES OF CATALYSTS

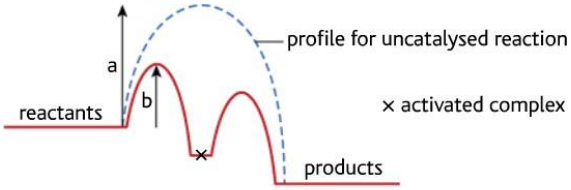


In the upward slope, the reactant molecules are coming together and breaking apart. Separating atoms in the reactant molecules requires bonds to be broken, so this part of the reaction **absorbs** energy.

In the downward slope, the product molecules are forming and moving apart. Producing product molecules involves forming bonds, so this part of the reaction **releases** energy.

Many reactions appear not to take place at room temperature – the particles involved don't have sufficient energy when they collide to overcome the activation energy barrier. Activation energy is the minimum energy required to start a reaction by breaking bonds.

A catalyst speeds up a reaction by providing an alternative path with a lower activation energy. Lowering the activation energy increases the proportion of molecules with enough energy to react, however, it does not alter the average kinetic energy of the molecules.



a activation energy of uncatalysed reaction
b activation energy of catalysed reaction

A catalyst changes the mechanism of a reaction and makes a reaction more productive by increasing the yield of the desired product and reducing waste. One of the ways in which a catalyst can change the mechanism of a reaction is to combine with the reactants to form an intermediate. The intermediate is a stage in the transition from reactants to products. It breaks down to give the products and the catalyst is released. This frees the catalyst to interact with further reactant molecules and the reaction continues.

Catalysts can be divided into two types – homogenous catalysts and heterogeneous catalysts.

Process	Reactants	Catalyst	Type of catalyst
Haber synthesis	Nitrogen, hydrogen	Iron	Heterogeneous
Catalytic converter on car	Exhaust gases	Platinum	Heterogeneous
Contact process	Sulfur dioxide, oxygen	Vanadium(V) oxide	Heterogeneous
Esterification	Solutions of acid, alcohol	Hydrogen ions	homogenous

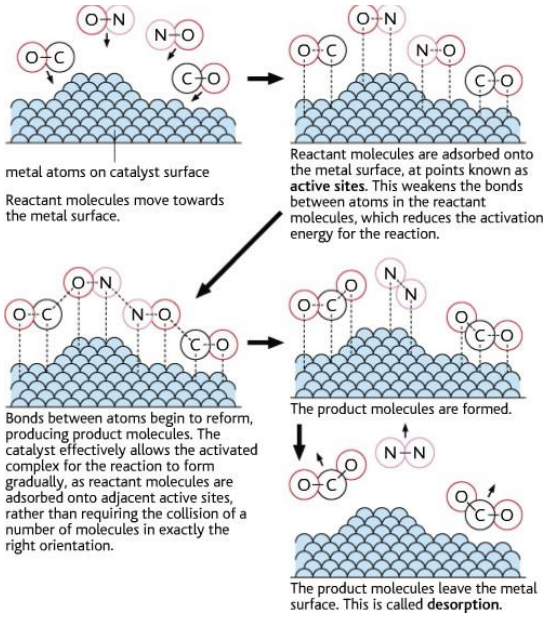
Homogenous catalysts

A homogeneous catalyst is in the same phase as the reactants. Chlorine free radicals act as a homogenous catalyst in the gas phase. Chlorine free radicals are produced when UV light from the Sun breaks up chlorine molecules. They are breaking down ozone in the upper atmosphere into oxygen.

$$Cl\bullet\ (g) + O_3(g) \rightarrow ClO\bullet\ (g) + O_2(g)$$
$$ClO\bullet\ (g) + O_3(g) \rightarrow Cl\bullet\ (g) + 2O_2(g)$$

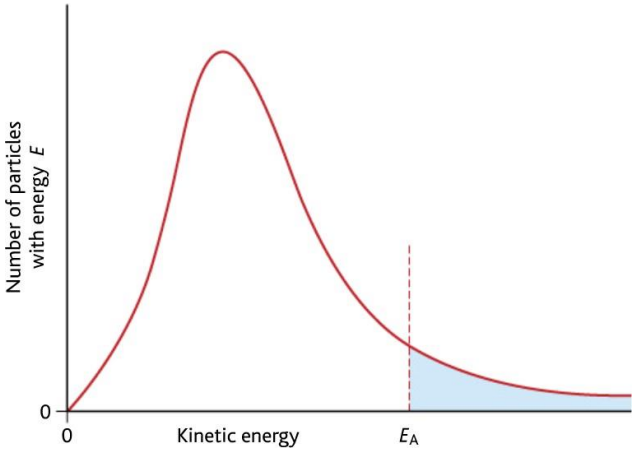
Heterogeneous catalysts

A heterogeneous catalyst is in a different phase from the reactants. Heterogeneous catalysts are frequently transition metals – for example iron, platinum and nickel. The reacting mixtures are usually adsorbed onto the surface of the catalyst, so the catalyst is usually given a very large surface area to maximise its effect on the reaction rate.


metal atoms on catalyst surface
Reactant molecules move towards the metal surface.
Reactant molecules are adsorbed onto the metal surface, at points known as **active sites**. This weakens the bonds between atoms in the reactant molecules, which reduces the activation energy for the reaction.
Bonds between atoms begin to reform, producing product molecules. The catalyst effectively allows the activated complex for the reaction to form gradually, as reactant molecules are adsorbed onto adjacent active sites, rather than requiring the collision of a number of molecules in exactly the right orientation.
The product molecules are formed.
The product molecules leave the metal surface. This is called **desorption**.

8 THE ARRHENIUS EQUATION

The diagram shows a distribution of the kinetic energies of particles in a sample of gas at a constant temperature. In this graph, E_A represents the activation energy. The area under the curve represents the total number of particles and the shaded area under the curve represents the number of particles with sufficient energy to react.



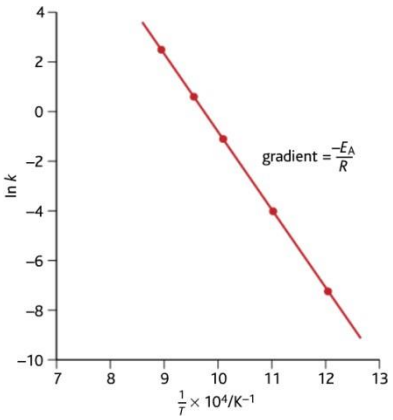
Using the kinetic theory and probability theory, it can be shown the fraction of molecules with greater energy than E_A is given by $e^{E_A/RT}$, where R is the gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature and e is the exponential constant. From this we can say that at a given temperature:

$k = Ae^{EA/RT}$

A is called the Arrhenius constant.

Applying logarithms:

$$\ln k = -\frac{E_A}{RT} + \ln A$$



A straight line can be represented by y = mx + c. So, a graph of ln k against $\frac{1}{T}$ is a straight line graph, the gradient is $\frac{EA}{R}$ and the y-intercept is the value for the Arrhenius constant, A, for the reaction.

9 RELATING A MECHANISM TO THE RATE-DETERMINING STEP

Rate equations were one of the first pieces of evidence to set chemists thinking about the mechanism of reactions. They wanted to understand why a rate equation cannot be predicted from the balanced equations for the reaction. The conclusion they reached was that most chemical reactions take place in a series of steps. The different steps in a multi-step process have different speeds. In a multi-step reaction, the slowest step is called the rate-determining step and this determines the speed of the overall reaction.

Kinetic measurements establish the order of the reaction for each species. For a reaction between A, B and C the rate equation could be:

$$\text{Rate} = k[A][C]^2$$

Since substance B does not occur in the rate equation, any step involving molecule B must be fast. This rate equation demonstrates that:

- The reaction is first order with respect to A – so A is involved in the rate-determining step.
- The reaction is second order with respect to substance C – so two moles of C are involved in the rate-determining step.

A reaction: Decomposition of ammonia

In the presence of a hot platinum catalyst, this is a zero order reaction. Ammonia rapidly diffuses to the surface of the metal and is adsorbed onto the surface. This happens fast. Bonds break and atoms rearrange to make new molecules on the surface of the metal. This is the slowest process and is the rate-determining step. The rate of reaction is determined by the surface area of the platinum.

Hydrolysis of halogenoalkanes

Two substitution mechanisms possible when a halogenoalkane reacts with aqueous alkali:

$$R – X + OH^- \rightarrow R – OH^- + X^-$$

Only the experimental data can show which mechanism actually takes place.

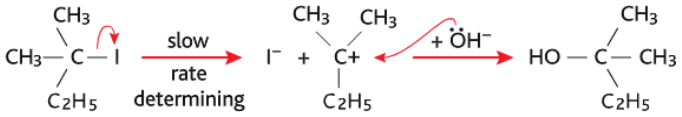


fig. 1.1.27 The S_N1 substitution reaction mechanism.

- The C – halogen bond breaks first followed by attack by the hydroxide ion.
- The slow step involves only one species and does not depend on the concentration of hydroxide ions. Hence the reaction is first order overall:

$$\text{Rate} = k[RI]$$

This is called S_N1 mechanism → substitution/nucleophilic/first order or unimolecular.

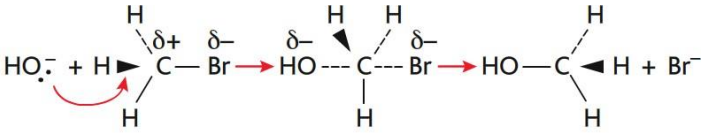


fig. 1.1.28 The S_N2 substitution reaction mechanism.

- The single step illustrated for the substitution of 1-iodopropane, a primary halogenoalkane, involves two different species – both the hydroxide ion and the primary halogenoalkane.
- The reaction will be second order – it depends on the concentration of both the hydroxide ion and the primary halogenoalkane.

$$\text{Rate} = k[RX][OH^-]$$

This is called S_N2 mechanism → substitution/nucleophilic/second order or bimolecular.

The reaction mechanism must be consistent with evidence:

- If the reaction is second order overall it must involve two different species.
- If the reaction is first order overall them this is the rate-determining step and it must be a two-step reaction.

Sample kinetic data as evidence for S_N1 and S_N2 reaction mechanisms:

Concentration of bromoalkane A /mol dm^{-3}	Concentration of hydroxide ions /mol dm^{-3}	Initial rate /mol dm^{-3} s^{-1}	Concentration of bromoalkane B /mol dm^{-3}	Concentration of hydroxide ions /mol dm^{-3}	Initial rate /mol dm^{-3} s^{-1}
0.1	0.1	1.11×10^{-5}	0.1	0.1	1.50×10^{-5}
0.2	0.1	2.22×10^{-5}	0.2	0.1	3.00×10^{-5}
0.3	0.1	3.33×10^{-5}	0.3	0.1	4.50×10^{-5}
0.1	0.2	1.11×10^{-5}	0.1	0.2	3.00×10^{-5}
0.1	0.3	1.11×10^{-5}	0.1	0.3	4.50×10^{-5}

10 MECHANISM OF THE REACTION OF IODINE WITH PROPANONE

Iodine and propanone react, in the presence of acid, in a substitution reaction to form iodopropane. The reaction can be represented by:

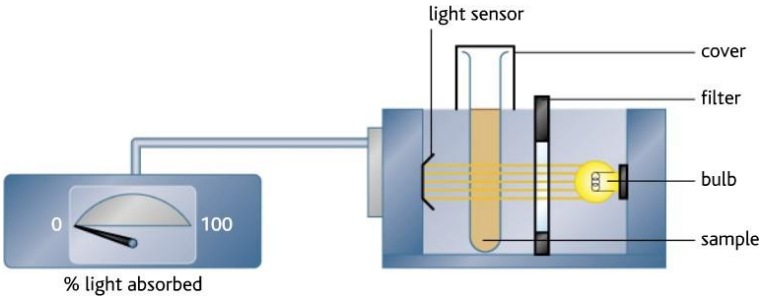
$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_2ICOCH_3(aq) + H^+(aq) + I^-(aq)$$

Kinetic experiments can be carried out using different concentrations of propanone, iodine and hydrogen ions.

Using colorimeter

A colorimeter measures the absorption of light during the progress of the experiment. First, the colorimeter has to be calibrated using standard iodine solutions. The reaction mixture containing iodine will be light brown in colour and as the reaction proceeds the solution becomes paler and more light is transmitted.

Note: the chosen filer should let through only the wavelength to be absorbed by the coloured iodine solution. Since iodine solution is brown-red, a blue-green filter is used.



Experiment	$[CH_3COCH_3]$ /mol dm^{-3}	$[I_2]$/mol dm^{-3}	$[H^+]$/mol dm^{-3}	Relative rate
1	0.1	0.1	0.1	2
2	0.1	0.2	0.1	2
3	0.1	0.2	0.2	4
4	0.2	0.1	0.1	4
5	0.1	0.1	0.2	4

By titration

During the experiment small aliquots (samples) of the reaction mixture are removed with a pipette.

The withdrawn sample is put in a flask and excess sodium hydrogencarbonate is added. This effectively stops the reaction so no further change in iodine concentration occurs during titration. The aliquots are titrated with a standard solution of sodium thiosulfate using starch indicator near the end-point. The measured values for the $[I_2]$ can be used to calculate the concentrations of the other substances involved. **Table 1.1.9** summarises the results of such an experiment. We can conclude that:

- doubling the concentration of iodine has no effect on the relative rate of the reaction (experiments 1 and 2)
- doubling the concentration of propanone doubles the relative rate of the reaction (experiments 1 and 4)
- doubling the concentration of hydrogen ions doubles the relative rate of the reaction (experiments 1, 3 and 5).

Using this we can write the rate equation:

$$\text{rate} = k[CH_3COCH_3][H^+]$$

The reaction is first order with respect to propanone and hydrogen ions, but zero order with respect to iodine. The overall order of the reaction is two. What does this tell us about the mechanism of the reaction?

The reaction involves various steps and the slowest step, the rate-determining step, does not involve iodine. This is why iodine does not appear in the rate equation. Hydrogen ions act as a catalyst – they are regenerated during the reaction.

A possible mechanism for the reaction of iodine and propanone in acid solution is given below.

Step 1

An H^+ ion protonates the oxygen atom in propanone:

$$(CH_3)_2C{=}O + H_3O^+ \rightleftharpoons (CH_3)_2C{=}O^+H + H_2O$$

This is a reversible reaction involving proton transfer (acid–base reaction). Remember that a protonated water molecule, H_3O^+, behaves as an H^+ ion.

Step 2

The electrons in the C=O bond partly shift to form a carbocation – i.e. the positive charge is transferred from the oxygen to the carbon:

$$(CH_3)_2C{=}O^+H \rightleftharpoons (CH_3)_2C^+{-}OH$$

Step 3

This carbocation loses a proton and *slowly* changes into the ***enol*** form. The enol has both alkene and alcohol functional groups and is **isomeric** with the original ketone:

$$(CH_3)_2C^+{-}OH + H_2O \rightleftharpoons CH_3C(OH){=}CH_2 + H_3O^+$$

This involves breaking a strong C–H bond, hence this step has a high activation energy and slow speed. The positive charge on the adjacent carbon of the carbocation facilitates in 'pulling' the C–H bond pair to form the C=C bond and releases the proton to form an H_3O^+ ion.

The rate of formation of the enol thus depends on the concentrations of the ketone and the acid.

Step 4

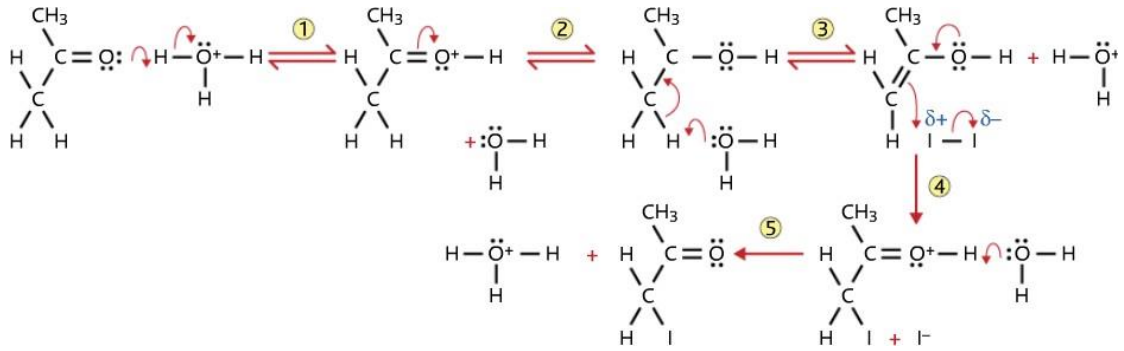
The iodine molecule acts as an **electrophile** and undergoes a quick **electrophilic addition reaction** (like other alkenes). This produces a protonated iodoketone:

$$CH_3C(OH){=}CH_2 + I_2 \rightarrow CH_3C(=O^+H){-}CH_2I + I^-$$

Step 5

A water molecule then rapidly removes the proton in another acid–base reaction to form the iodoketone:

$$CH_3C(=O^+H){-}CH_2I + H_2O \rightarrow CH_3COCH_2I + H_3O^+$$



How far? - entropy

1 THERMODYNAMICS

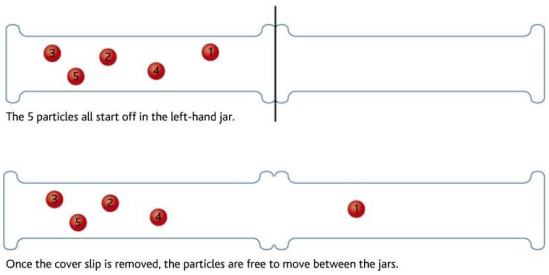
The interaction of energy and matter governs our lives. Thermodynamics is study of the two and their interaction. It deals with the laws of heat energy, and its transfer to other types of energy. Thermodynamics has 3 laws…

The first law of thermodynamics states that **energy can never be created or destroyed**.

The second law of thermodynamics states that **entropy always increases in the transformation of energy**.

The second law of thermodynamics – disorder and entropy

The process of diffusion is helpful to comprehend entropy. The diagram shows a simplified situation with 5 particles (bromine molecules) undergoing diffusion.


The 5 particles all start off in the left-hand jar.
Once the cover slip is removed, the particles are free to move between the jars.

Each particle has two possible ways of being arranged – in the left-hand jar or in the right-hand jar. If we represent the number of possible arrangements for particle 1 as W_1, for particle 2 as W_2 and so on, then the *total* number of ways, W, that the five particles can be arranged between the two jars is given by:

$$W = W_1 \times W_2 \times W_3 \times W_4 \times W_5$$
$$= 2 \times 2 \times 2 \times 2 \times 2$$
$$= 2^5$$
$$= 32$$

And for a real situation where there will be something like 10^{22} particles, W has an enormous value (2^{220}) and only 2 of these arrangements have all the particles in one jar; so we are quite justified in saying that **gases always spread out**.

2 ENTROPY

Entropy: Random dispersal of molecules and of energy quanta between molecules.

Unit: J mol^{-1} K^{-1}

Entropy (symbol S) is a measure of disorder in a system. You can also think of it as a dispersal or spreading of energy between particles in system, or between a system and its surroundings.

Molecules and energy

It is not only the arrangement of molecules that matters. Even more important is the way that energy is spread out between molecules. The molecules in bromine gas are moving around, spinning and vibrating. The energies of tiny molecules are quantised, in a similar way to the energies of electrons in atoms. All the time the molecules are bumping into each other and as they do so they lose and gain energy quanta to and from other molecules.

The more molecules, and the more energy quanta, the more ways there are of sharing the energy between the molecules. Increasing the temperature of a substance increases the number of energy quanta in the system and so increases the number of possible ways that the energy quanta can be shared out between the molecules.

3 STANDARD MOLAR ENTROPY AND CHANGE OF STATE

Standard molar entropy is the entropy per mole for a substance under standard conditions. It is quoted for pure chemicals under standard conditions (298K and 1 atmospheric pressure).

The third law of thermodynamics states that **perfect crystals at zero Kelvin have zero entropy**.

- This means that in a perfect crystal, at absolute zero, nearly all molecular motion should cease in order to achieve $\Delta S = 0$. A perfect crystal is one in which the internal lattice structure is the same at all times – in other words, it is fixed and non-moving, and the particles are neither rotating nor vibrating in their positions.

Changes in entropy with change of state

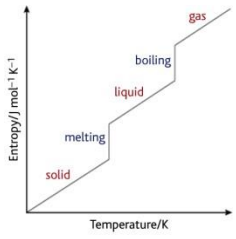


fig. 1.2.6 The changes in entropy that accompany changes in state.

The entropy of a chemical rises as the temperature rises. Increasing the temperature raises the number of energy quanta to share between the atoms and molecules. There are also jumps in the entropy of a chemical wherever there is a change of state. This is because energy is added to change a solid to a liquid or a liquid to a gas. Also there is an increase in the number of ways of arranging the atoms or molecules as a solid changes to a liquid, then to a gas.

Solids → Solids have relatively low values for standard molar entropies. The heavier, larger atoms can vibrate more freely and share out their energy in more ways.

Liquids → In general, liquids have higher standard molar entropies than comparable solids because the atoms or molecules are free to move. Molecules with more atoms (more complex molecules) have higher standard molar entropies because they can vibrate, rotate and arrange themselves in yet more ways.

Gases → Gases have even higher standard molar entropies than comparable liquids because the atoms or molecules are not only free to move but are also widely spaced. As with liquids, molecules with more atoms have even higher standard molar entropies because they can vibrate, rotate and arrange themselves in more ways.

In summary: The standard entropy of a substance depends mainly on its physical state but also on its complexity.

4 THE NATURAL DIRECTION OF CHANGE

Reaction kinetics and spontaneity

A spontaneous reaction is one which tens to go without being driven by any outside agency. (However, it gives no indication of rate.)

Just as a stone tends to run downhill, energy tends to run downhill. The low energy state of the products is more stable than the higher energy state of the reactants. Therefore, it may be reasonable to assume exothermic reactions are favourable and spontaneous whereas endothermic reactions are not, thus to say that enthalpy changes govern whether reactions occur.

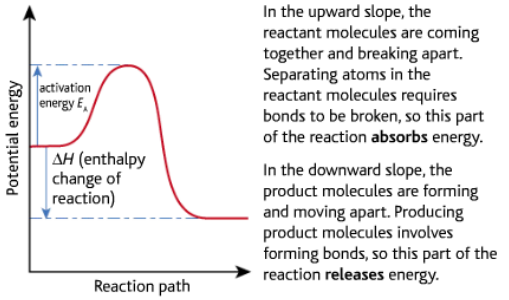

Potential energy
activation energy E_a
ΔH (enthalpy change of reaction)
Reaction path
In the upward slope, the reactant molecules are coming together and breaking apart. Separating atoms in the reactant molecules requires bonds to be broken, so this part of the reaction **absorbs** energy.
In the downward slope, the product molecules are forming and moving apart. Producing product molecules involves forming bonds, so this part of the reaction **releases** energy.

fig. 1.2.7 **Before reactants can become products, the activation energy has to be supplied.**

Spontaneity and entropy

Much to our surprise, **there are some spontaneous endothermic reactions**. Since endothermic reactions can occur spontaneously at room temperature, **enthalpy changes alone do not control whether reactions occur**. But enthalpy change is, without a doubt, one of the most important factors determining the spontaneity of a reaction.

Reactions occur due to chance collisions, and one possible ordered arrangement, can be rearranged into many possible disordered arrangements, so the **probability of disorder is greater than order**.

Therefore, the other thing that favours a reaction being spontaneous is an increase in the system's entropy.

- All reactions that are highly exothermic and lead to greater disorder are spontaneous at all temperatures.
- Any reaction that is neither of these is never spontaneous.

The natural direction of change is in the direction of increasing total entropy (positive entropy change). This total entropy depends on both the enthalpy change of the reaction and the entropy change in the system.

5 INVESTIGATING CHEMICAL REACTIONS QUALITATIVELY

You can apply some basic principles that suggest the direction of the entropy change in a reaction.

- Ions and molecules usually have higher entropies in solution than they do as solids.
- Gases usually have higher entropies than liquids or solids, so if a gas is produced it is likely that the overall entropy will increase.
- When large molecules break down into smaller molecules entropy increases. This is because there are far more ways of arranging several small molecules than a big one.

6 CALCULATING ENTROPY CHANGES

Calculating ΔS_{system}

It is calculated by subtracting the total standard entropy of the reactants than that of the products.

$$\Delta S^{\ominus}_{\text{sys}} = \Sigma S^{\ominus}_{\text{products}} - \Sigma S^{\ominus}_{\text{reactants}}$$

Calculating $\Delta S_{surroundinRs}$

To calculate the entropy change of the surroundings, we need to know the energy transferred to them, which is given by the change in enthalpy. The entropy change is calculated from the relationship:

$$\Delta S_{surr} = -\frac{\Delta H}{T}$$

Where T is the absolute temperature.

The entropy change of the surroundings depends on temperature, with the transfer of a given quantity of energy to surroundings at low temperature producing a greater entropy change than the transfer of the same amount of energy to the surroundings at a higher temperature.

Calculating ΔS_{total}

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

As discussed, feasibility of a reaction depends on the total entropy change. A positive ΔS_{total} means that the reaction is feasible. Therefore, the feasibility of a reaction depends on the balance between ΔS_{system} and $\Delta S_{surroundinRs}$, and at higher temperatures the magnitude of $\Delta S_{surroundinRs}$ decreases and its contribution to ΔS_{total} is less.

Reactions can occur as long as ΔS_{total} is positive even if one of the other entropy changes is negative.

		ΔH	
		Positive	**Negative**
ΔS_{sys}	**Positive**	spontaneous only at high temperatures	always spontaneous
	Negative	never spontaneous	spontaneous only at low temperatures

Entropy, free energy and spontaneous change

The relationships:

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

and

$$\Delta S_{surr} = -\Delta H / T$$

can be combined to produce the relationship:

$$\Delta S_{total} = \Delta S_{sys} - \Delta H / T$$

Multiplying this relationship by T gives:

$$T\Delta S_{total} = T\Delta S_{sys} - \Delta H$$

or

$$-T\Delta S_{total} = \Delta H - T\Delta S_{sys}$$

The quantity $-T\Delta S_{total}$ is called the **Gibbs free energy** change, or ΔG, named after the American scientist Josiah Willard Gibbs. Under standard conditions, the standard free energy change for a reaction is given by:

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}_{sys}$$

Since ΔS_{total} must be positive for a change to occur spontaneously, it follows that such changes have ΔG less than zero (in other words, negative).

7 THERMODYNAMIC STABILITY AND KINETIC INERTNESS

Some reactions are puzzling because they are highly exothermic but are not spontaneous at room temperature.

There are different kinds stability that can affect chemical reactions. The thermodynamic stability of a compound relative to its elements depends on the enthalpy level of the products relative to the reactants. For exothermic reactions, a negative enthalpy of formation indicates that a compound is more stable than its elements.

A chemical reaction is feasible when ΔS_{total} has a positive value. However, this tells us nothing at all about the rate of reaction. A high activation energy barrier may prevent a reaction starting. In such cases, the reactants are kinetically stable or kinetically inert.

Energy must first be provided to start such reactions, for example:

- A spark
- Heat
- Light

A chemical or mixture is thermodynamically stable if there is no tendency for a reaction. If the total entropy change is negative, this indicates that the reaction does not tend to occur.

Kinetic inertness is a term used when a reaction does not go even though it appears to be feasible. The reaction tends to go as indicated by the positive total entropy change, yet nothing happens. There is no change because the rate of reaction is too slow to be noticeable. A high activation energy prevents the reaction.

ΔS_{total}	Activation energy	Change observed
Negative	High	No reaction – reactants stable relative to products
Positive	High	No reaction – reactants kinetically inert (but unstable)
Negative	Low	No reaction – reactants stable relative to products
Positive	low	Fast reaction – reactants unstable relative to products

8 PREDICTING SOLUBILITY OF IONIC COMPOUNDS

When ionic solids, such as sodium chloride, dissolve in a polar solvent, there are two separate enthalpy terms from two separate processes:

- Lattice energy – the solid must separate into individual ions to dissolve (an endothermic change).
- Hydration enthalpy – the separated ions interact with the surrounding polar solvent, such as water (an exothermic change).

The enthalpy of solution of an ionic compound is:

$$\Delta H_{solution} = -\Delta H_{lattice\ energy} + \Delta H_{hydration}$$

When a new lattice forms from gaseous ions, energy is released in an exothermic process. This is lattice energy. When a crystalline material dissolves, the reverse happens. An amount of energy numerically equal to the lattice energy must be put in to break the crystal and separate the ions. This is an endothermic process.

$\Delta H_{solution}$ can have a positive or negative value.

- A positive $\Delta H_{solution}$ corresponds to an overall endothermic change – dissolving is not favoured. It may still be favoured by an increase in entropy. Solid sodium chloride is a highly ordered 3-D lattice with a low entropy value. On dissolving, the ions separate and move independently; the entropy of the system therefore increases, favouring the change.
- A negative $\Delta H_{solution}$ corresponds to an overall exothermic change and so dissolving is favoured in terms of both enthalpy and entropy.

Calculating enthalpy of hydration or solution from Hess cycles

The standard enthalpy of hydration of an ion is the enthalpy change when one mole of gaseous ions is hydrated under standard conditions, where further dilution would cause no further enthalpy change, sometimes called infinite dilution. For example:

Na^+ (g) + aq → Na^+ (aq)

It is not possible to measure such enthalpy changes directly because ionic compounds contain both cations and anions together. We use a Hess's law cycle to find the enthalpy of hydration.

Factors affecting the enthalpy of hydration and the lattice energy

The lattice enthalpy of a compound is affected by:

- The charge on the ions – larger charges increase the force of attraction between oppositely charged ions
- The size of ions – smaller ions fit closer and this increases the force of attraction
- The degree of covalency in the ionic bonding – whether the bonding is 100% ionic and the ions completely separate, as the ionic model assumes.

Hydration enthalpy is affected by:

- Ionic radius – small ions have a greater charge density
- Ionic charge – larger charges increase the charge density

Ions with high charge densities attract more polar water molecules giving more ion-dipole interactions. These interactions are exothermic and the system shows a decrease in enthalpy.

Experimental values of lattice energy determined from Born-Haber cycles compared to theoretical values can identify a degree of covalent character in ionic compounds. A mismatch identifies polarization of the anion with a degree of covalent character.

Equilibria

1 Dynamic equilibrium

Many reactions, including important industry reactions, are reversible. They end towards a state of balance. This is known as the equilibrium for the reaction. However, this equilibrium is not static but rather dynamic.

In dynamic equilibrium the forward and backwards changes continue at **the same rate** so that overall there is no change. At the molecular level there is continuous activity. At the macroscopic level nothing appears to be happening.

Dynamic equilibrium does not only apply to chemical reactions but also to physical changes such as change in the state of matter or dissolving a substance.

Example 1: If a block of ice is put into water at 0°C and the conditions kept constant, both the ice and the water remain. However, the melting and freezing processes continue at equal rates.

Example 2: When salt is added to water, the salt dissolves to form a solution. As more salt is added, the solution becomes more concentrated, until eventually a saturated solution is formed when no more salt appears to dissolve in the water. However, there is a state of dynamic equilibrium. Sodium ions and chloride ions are leaving the solid and entering the solution at the same rate as sodium ions and chloride ions are entering the crystals from the solution.

2 Hydrogen-Iodine equilibrium

When hydrogen and iodine are first mixed in a closed system, the forward reaction alone begins since there are no products present. As the amounts of reactants fall, the forward rate decreases. Once some product molecules have been formed, the reverse reaction can begin. The rate of the reverse reaction increases until forward and reverse reactions are happening at the same rate. This is a dynamic equilibrium at a constant temperature.

Expt.	Initial concentration/mol dm^{-3}			Equilibrium concentration/mol dm^{-3}		
	$[H_2(g)]$	$[I_2(g)]$	$[HI(g)]$	$[H_2(g)]$	$[I_2(g)]$	$[HI(g)]$
1	0.0442	0.0364	0	0.0132	0.0054	0.0620
2	0.0442	0.0288	0	0.0181	0.0027	0.0510
3	0.0334	0.0288	0	0.0093	0.0047	0.0482
4	0	0	0.0518	0.0050	0.0050	0.0366

table 1.3.1 Initial and equilibrium concentrations of hydrogen, iodine and hydrogen iodide in several experiments.

By considering the values given in the table, it is possible to identify the relationship between the reactant and the product equilibrium concentrations at a particular temperature.

The relationship,

$$K_c = \frac{[HI(g)]^2_{eq}}{[H_2(g)]_{eq}[I_2(g)]_{eq}}$$

is called the equilibrium expression for the reaction between hydrogen and iodine, and the result is called the equilibrium constant for the reaction. It has a value of 54 for this reaction when it is carried out at 700 K. If the value is anything else, then the mixture is not at equilibrium, and the gases will react further until an equilibrium exists.

Expt. 1	Expt. 2	Expt. 3	Expt. 4
53.9	53.2	53.2	53.6

3 THE EQUILIBRIUM LAW

The equilibrium law for a particular reaction can always be predicted from its stoichiometric equation. The general equilibrium for substances A, B, C and D:

$$aA + bB \rightleftharpoons cC + dD$$

has the equilibrium law:

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

This value of K_c is valid only for the forward reaction. The equilibrium constant of the backward reaction is the reciprocal of the equilibrium constant for the forward reaction. In other words:

$$K_c' = \frac{1}{K_c}$$

Units and the equilibrium constant

The units of equilibrium constant may be different for different reactions. It depends on the stoichiometry of a particular reaction.

4 EQUILIBRIUM PARTIAL PRESSURES

For gases it is often more convenient to use their partial pressure rather their concentration.

Partial pressure: This is the pressure that the gas would have if it occupied the volume alone.

The partial pressure of gas A, in a mixture of gases A, B, C and D is calculated by:

$$p_A = \frac{\text{number of moles of A}}{\text{total number of moles in the mixture}} \times \text{total pressure}$$

$$= \frac{n_A}{n_A + n_B + n_C + n_D} \times p_{tot}$$

Suppose we have this reaction involving gases:

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

We can write the equilibrium expression using partial pressures:

$$K_p = \frac{p(C)^c \times p(D)^d}{p(A)^a \times p(B)^b}$$

- Partial pressure is used for mixtures of gases that do not react together chemically.
- We assume that each gas behaves independently in the gas mixture.
- The total pressure of the mixture is the sum of the partial pressures of each gas – this is Dalton's law of partial pressures.
- Partial pressure is defined in terms of mole fractions. For a mixture of two gases A and B,

$$the\ mole\ fraction\ of\ A = \frac{number\ of\ moles\ of\ A}{number\ of\ moles\ of\ A + B}$$

$$the\ partial\ pressure\ of\ A = mole\ fraction\ of\ A \times the\ total\ pressure\ of\ the\ system$$

Pressure units

- Atmospheres
- kPa
- mmHg
- N m^{-2}

5 HOMOGENEOUS AND HETEROGENEOUS EQUILIBRIA

Some equilibrium reactions involve only substances in the same phase e.g. all aqueous solutions or all gases. These are homogenous equilibria.

Some equilibrium reactions involve substances in different phases e.g. a pure liquid and a gas or a solid and a gas. These are heterogeneous equilibria.

Expressions for K_c and K_p do not include values for solid and pure liquid phases in heterogeneous reactions.

In general, the equilibrium expression for a heterogeneous reaction is written in such a way that the concentrations of solids and liquids are included in the equilibrium constant.

6 PREDICTING THE EXTENT OF REACTIONS

The equilibrium constant for a reaction, whether we use K_c or K_p, is a measure of how far a reaction proceeds to completion.

Value of K	Extent of reaction	
Very large $K > 1 \times 10^{10}$	Reaction proceeds almost to completion, leaving very small amounts of reactants at equilibrium	$C(s) + O_2(g) \rightleftharpoons CO_2(g)$
around 1	Concentrations of reactants and products are nearly the same at equilibrium	$2BrCl \rightleftharpoons Br_2 + Cl_2$ (in CCl_4 solution)
Very small $K < 1 \times 10^{-10}$	Reaction hardly occurs, producing very small quantities of products at equilibrium	$2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$

When we look at reactions and their equilibrium constants, the term position of equilibrium is often used. When a reaction has a large equilibrium constant, the position of the equilibrium is said to lie on the right-hand side of the equation; for a reaction with a small equilibrium constant the equilibrium lies well to the left.

Finally, note that the equilibrium constant tells us nothing about the rate of a reaction. Even if the equilibrium constant for a reaction is very large, the rate at which it happens may be extremely slow. For example, a mixture of hydrogen and oxygen does not spontaneously react to form water at room temperature.

7 DETERMINATION OF AN EQUILIBRIUM CONSTANT

The value for the equilibrium constant for a reaction can only be found by experiment. This will involve measuring the concentrations of reactants and products at equilibrium at a constant temperature.

Determining an equilibrium constant involves three basic steps:

- Combining known quantities of reactants under a carefully measured and controlled conditions and allowing the reaction to come to equilibrium at a fixed temperature.
- Measuring accurately the concentration of one (or more) of the substances in the equilibrium mixture, and from this calculating the equilibrium concentrations of the other substances in the mixture.
- Substituting these equilibrium concentrations in the equilibrium expression and calculating the value.

These steps should be repeated using different initial concentrations to confirm the valueof the equilibrium constant.

Hydrolysis of ethyl ethanoate

Different, known quantities of ethyl ethanoate and water are mixed and left to reach equilibrium. Without a catalyst the reaction may take several years to reach equilibrium. A small quantity of hydrochloric acid is added to each reaction mixture to act as a catalyst.

If the initial numbers of moles of ethyl ethanoate and water were x, and the number of moles of ethanoic acid was y, then at equilibrium, the amount of each substance is:

$$\underset{(x-y)\text{mol}}{CH_3COOC_2H_5(l)} + \underset{(x-y)\text{mol}}{H_2O(l)} \rightleftharpoons \underset{y\text{mol}}{CH_3COOH(l)} + \underset{y\text{mol}}{C_2H_5OH(l)}$$

If the volume is $V\text{dm}^3$, then the concentrations are $\frac{(x-y)\text{mol}}{V\text{dm}^3}$, $\frac{(x-y)\text{mol}}{V\text{dm}^3}$, $\frac{y\text{mol}}{V\text{dm}^3}$ and $\frac{y\text{mol}}{V\text{dm}^3}$, respectively.

$$K_c = \frac{[CH_3COOH(l)]\ [C_2H_5OH(l)]}{[CH_3COOC_2H_5(l)]\ [H_2O(l)]}$$

$$= \frac{y/V\ \text{mol dm}^{-3} \times y/V\ \text{mol dm}^{-3}}{(x-y)/V\ \text{mol dm}^{-3} \times (x-y)/V\ \text{mol dm}^{-3}}$$

$$= \frac{y^2}{(x-y)^2}$$

Note that because the number of moles of reactants and products are the same, the volume V cancels out. This is not always the case – and you must use concentrations and not numbers of moles in the calculation.

Distribution of iodine between two immiscible liquids

Hexane and water are immiscible liquids. When added together, they form separate layers with hexane floating on the water. If some iodine is added, it will dissolve in both the hexane layer and the water layer, although it is relatively insoluble in water.

$$I_2(\text{hexane}) \rightleftharpoons I_2(\text{water})$$

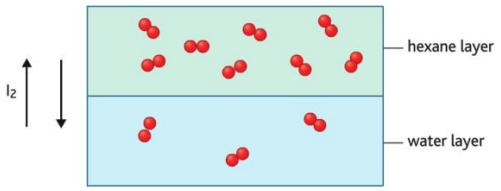


fig. 1.3.9 A dynamic equilibrium is set up as the iodine moves between the two solvents.

A known quantity of iodine is added to a known volume of hexane and water, and the system is allowed to come to equilibrium. The equilibrium concentration of iodine in the water layer can be found by titration with standard sodium thiosulfate solution. Knowing the original amount of iodine enables the concentration of iodine in the hexane layer to be calculated. The equilibrium constant for this reaction is called the partition constant, K_{part}:

$$K_{part} = \frac{concentration\ of\ iodine\ in\ hexane}{concentration\ of\ iodine\ in\ \text{mater}}$$

8 ENTROPY AND THE EQUILIBRIUM CONSTANT

There is a problem with applying the idea of entropy to a dynamic equilibrium because there are two different reactions going on at the same time:

$$reactants \rightleftharpoons products$$

For such reversible systems:

- Both the forward and the backward reactions are spontaneous and so ΔS_{total} must be positive in both cases.
- The balance between the amounts of reactants and products is determined by the equilibrium constant K.
- The total entropy change, $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundinRs}$, is zero at equilibrium.

Note it is the total entropy change that is zero at equilibrium, not the total entropy. In fact, total entropy of the system is a maximum at equilibrium – **any change from this position would result in a decrease in total entropy**.

The relationship between these quantities is given by:

$$\Delta S_{\text{total}} = R \ln K$$

R is the gas constant and K is the equilibrium constant (either K_c or K_p). Since R is a constant, an increase in ΔS_{total} results in an increase in the equilibrium constant K as well.

Hence, the total entropy change not only indicates the spontaneous direction of a reaction, but also the extent to which it takes place (how far it goes to completion). The larger the positive value of the total entropy change, the larger the value of K, and so further the equilibrium position shifts towards the products.

Using entropy to explain the effect of temperature on an equilibrium constant

Both exothermic and endothermic reactions affect the entropy of the surroundings.

- Exothermic reactions release energy to the surroundings.
- $\Delta S_{surr} = -\frac{\Delta H}{T}$

The convention for enthalpy changes is that ΔH is negative for an exothermic change. This double negative makes the value of $\Delta S_{surroundinRs}$ positive, in other words it goes up.

- Exothermic reactions increase the entropy of the surroundings.

$\Delta S_{total} = R \ln K$ can be written as $\ln k = \left(\frac{1}{R}\right) \times (\Delta S_{system} + \Delta S_{surroundinRs})$

$$\ln k = \left(\frac{1}{R}\right) \times \left(\Delta S_{system} - \frac{\Delta H}{T}\right)$$

- When the temperature is raised, the magnitude of $-\frac{\Delta H}{T}$ decreases.

- For an exothermic reaction, as T increases, ln K becomes smaller (this means less product in the reaction, as predicted by le Chatelier's principle).
- For an endothermic reaction, as T increases, ln K becomes larger.
- The increase of $\Delta S_{surroundinRs}$ becomes less significant and the position of equilibrium shifts.
- When the temperature is raised, for an endothermic reaction the significant factor is the increase in ΔS_{system}.

Hence:

- For an exothermic reaction, when T increases, K decreases.
- For an endothermic reaction, when T increases, K increases.

Application of rates and equilibrium

1 FACTORS THAT AFFECT EQUILIBRIA

Effect of catalysts on equilibrium and rate

- Catalysts speed up both forward and reverse reactions.
- Catalysts lower the activation energy.
- Catalysts reduce the time taken to establish equilibrium.
- Catalysts have no effect on the value of the equilibrium constants.

Effect of temperature changes on equilibrium and rate

Reversible reactions will be exothermic in one direction and endothermic in the reverse direction. The temperature effects on yield can be summarised as follows:

- In a reaction where ΔH is positive, K rises with temperature increase, giving more of the products.
- When ΔH is negative, K falls with temperature increase, giving more reactants.
- Increased temperature increases the rate constant k, so the rate increases with increasing temperature.

Effect of concentration and pressure changes on equilibrium and rate

- Adding more reactants to an equilibrium mixture accelerates the forward reaction.
- As the amounts of products increase, the reverse reaction starts to speed up. A new position of equilibrium is established but the value of K remains unchanged.
- The pressure of a gas is proportional to its concentration. Changes of pressure also do not affect the value of K.
- A change in pressure affects the position of equilibrium according to le Chatelier's principle.
    - An increase in pressure, or a decrease in volume, tends to move the reaction in the direction that will decrease the number of moles of gas.

- A decrease in pressure, or increase in volume, tends to move the reaction in the direction that will increase the number of moles of gas.

- Increasing the pressure of a gas means that there are more molecules in a given volume (equivalent to an increase in concentration) so they collide more frequently, and the rate of a reaction increases.

2 THE ATOM ECONOMY IN INDUSTRY

$$atom\ economy\ (\%) = \frac{mass\ of\ atoms\ in\ the\ desired\ product}{total\ mass\ of\ atoms\ in\ reactants} \times 100\%$$

The atom economy, which is an important concept, can be improved by:

- Recycling unreacted reagents
- Using an alternative reaction
- Finding uses for any by-products

3 HSW – HABER SYNTHESIS FOR AMMONIA

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

ΔH = -90 kJ mol^{-1}

- The forward reaction producing ammonia is exothermic, so low temperatures will favour high yields of ammonia.
- However, low temperatures will decrease the rate of the reaction.
- The forward reaction causes a decrease in entropy because there are fewer product molecules than reactant molecules.
- The forward reaction should be spontaneous only at low temperatures – decrease in moles of gas, so there is negative entropy change.
- High pressure favours the forward reaction (increased yield of ammonia) because this lowers the number of gaseous molecules and the equilibrium moves as predicted by le Chatelier's principle.
- High pressure also increases the rate of reaction.
- However, it is expensive and potentially hazardous to the workforce to maintain very high pressures – energy cost and strong containers needed.

We have no information at all about the rate or the size of the activation energy. In fact, the uncatalysed reaction has a very high activation energy due to the strength of the triple bond in N_2 molecule, which must first be broken. The use of a catalyst provides an alternative route for a reaction with lower activation energy, which accelerates the rate of a reaction. The catalyst is iron.

The conditions chosen for industrial reactions are a compromise between an acceptable reaction rate (k) and reasonable equilibrium constant (K).

Acid/base equilibria

1 History of acidity

Ideas about the nature of acids and bases developed over centuries. Simple, early ideas bout acids included that they:

- Are corrosive liquids
- Have a sour taste
- Give characteristic colours with indicators

The understanding of acids has since been extended to include a wider range of materials. Acids in aqueous solution undergo some characteristic reactions. They react with:

- Bases giving a salt and water
- Carbonates to give a salt, water and carbon dioxide
- Some metals giving a salt and hydrogen

2 Arrhenius theory of acids

Arrhenius developed a theory of electrolytic dissociation. It states that when certain materials dissolve in water, they immediately split up from molecules into ions:

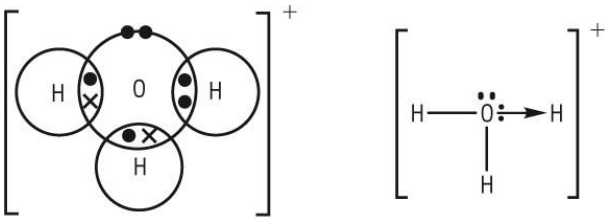
- Arrhenius acids give hydrogen ions H^+ in aqueous solution.
- Arrhenius bases give hydroxide ions OH^- in aqueous solution.

According to Arrhenius' theory, neutralisation occurs because the number of hydrogen ions from the acid is exactly equal to the number of hydroxide ions from the base, and so the two react completely to form water.

The theory could not be extended to include a wider range of materials.

The oxonium ion

Developments in understanding of the atom in the years following Arrhenius showed that it was almost inconceivable that the hydrogen ion could exist in solution independently. As a result, it was suggested that the H^+ ions exists in association with a water molecule as the H_3O^+ ion, called the oxonium ion.



$HA(aq) + H_2O(l) \rightarrow H_3O^+(aq) + A^-(aq)$

When talking about acids and bases, hydrogen ions are often referred to as protons. Strictly speaking, we should always remember that protons do not exist in solution and instead use the term oxonium ion, writing H_3O^+ instead of H^+.

HSW – Evidence for the H_3O^+ ion

Experimental evidence confirms the existence of H_3O^+ ion, since the positive ions in an acidic solution carrying an electric current move at a rate which is consistent with them having a size similar to that of a water molecule. If free H^+ ions did exist, the positive ions in acidic solutions would be expected to move much faster that this because of their small size.

3 THE BRØNSTED-LOWRY THEORY

Although it was useful, the problem with the Arrhenius definition of an acid was that it was limited to situations in which water was present, since it defined acids and bases in terms of the ions which were produced in aqueous solutions. There are many reactions which appear to be acid-base reactions that occur in solvents other than water, or even with no solvent at all. The new Brønsted-Lowry theory was based on the movement of protons. It applied to a wider range of examples than previous theories. It said that a Brønsted-Lowry:

- Acid is a substance that donates protons.
- Base is a substance that accepts protons.

Conjugate acid-base pairs

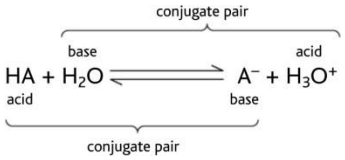
The Brønsted-Lowry theory defines an acid-base pair as follows:

- Two species that change into each other by gaining or losing a proton
- Each acid has a conjugate base
- Each base has a conjugate acid

As a result of the Brønsted-Lowry definition, when an acid dissociates, we can consider this to be an acid-base reaction that is in equilibrium:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

In the forward reaction, HA acts as an acid, donating a proton to a water molecule. Water, in accepting the proton, acts as a base. In the reverse reaction, the H_3O^+ acts as an acid, donating a proton to A^-, which of course acts as a base. In acid-base reactions it is always possible to find two acids and two bases. There are conjugate acid-base pairs.



- Strong Brønsted-Lowry acids have weak conjugate bases
- Weak Brønsted-Lowry acids have strong conjugate bases

4 pH AND DISSOCIATION CONSTANTS

In the nineteenth and early twentieth centuries, a number of scientists were working hard to find a way of indicating the degree of acidity or alkalinity of a solution. A person suggested the notation 'pH', standing for 'power of hydrogen' using the negative logarithm of the concentration of hydrogen ions in solution.

$pH = -\log[H^+(aq)]$

The ionic product of water K_w

In water, there is an equilibrium between the water molecules and the ions they dissociate into. This can be written as:

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Or more simply

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

We can write an expression for the equilibrium constant:

$$K_c = \frac{[H^+(aq)][OH^-(aq)]}{[H_2O(l)]}$$

This can be rewritten as:

$$K_c \times [H_2O(l)] = [H^+(aq)][OH^-(aq)]$$

Now, because the extent of dissociation into ions is small, it is reasonable to take $[H_2O(l)]$ as a constant. This means that K_C x $[H_2O(l)]$ is a constant – it is called the ionic product of water, K_w. At 298K:

$$K_w = [H^+(aq)][OH^-(aq)] = 1 \times 10^{-14}\,mol^2\,dm^{-6}$$

Note that, water therefore has a pH of 7 at room temperature but equilibrium constant will change with temperature. As the equilibrium constant changes, so does the pH. Increasing temperature increases the acidity of water.

K_a for acids

The strength of an acid or base is concerned with how good it is at donating or accepting protons. For an acid HA in aqueous solution the following equilibrium exists:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

A measure of the strength of an acid is the value of the equilibrium constant for its dissociation into ions – for the equilibrium above this is:

$$K_a = \frac{[H^+(aq)][A^-(aq)]}{[HA(aq)]}$$

The equilibrium constant for this reaction, K_a, is known as the dissociation constant of that acid. K_a provides a direct measure of the strength of the acid because it measures the extent of dissociation – **the larger the value the more dissociated the acid, and the greater its strength as a proton donor**. Because it is an equilibrium constant, the value of K_a is unaffected by changes in concentration, but it is affected by temperature. As the strength of the acid increases, the value of K_a also increases, thus the value for pK_a decreases.

The pK_a of an acid is also useful in another way. From the relationship between pK_a and K_a, we can write:

$$pK_a = -\log \frac{[H^+][A^-]}{[HA]}$$

$$= -(\log [H^+] + \log \frac{[A^-]}{[HA]})$$

So:

$$pK_a = pH - \log \frac{[A^-]}{[HA]}$$

This is significant because it means that $pK_a = pH$ when:

$$\log \frac{[A^-]}{[HA]} = 0$$

In other words, when:

$$\frac{[A^-]}{[HA]} = 1 \quad (\text{because } \log 1 = 0)$$

An acid is exactly 50% dissociated at a pH equal to its pK_a. This fits exactly with Brønsted-Lowry theory because, by definition, weaker acids have stronger conjugate bases, which will tend to be protonated at higher pH values. Stronger acids have weaker conjugate bases which will not tend to be protonated except at lower pH values.

5 Calculating pH from K_A and K_B

Strong acid

In a solution of a strong acid, we assume that the acid is 100% dissociated, so that **$[H^+(aq)]$ is equal to the concentration of the acid in the solution**.

Weak acid

We must use the concentration and the value of K_a to calculate the pH of a solution. To calculate the pH of a solution containing 0.5 mol dm^{-3} of methanoic acid ($K_a = 1.6 \times 10^{-4}$ mol dm^{-3}), we let $[H^+(aq)] = x$ mol dm^{-3}.

	$HCOOH(aq) \rightleftharpoons H^+(aq) + HCOO^-(aq)$		
Initial concentration ($mol\,dm^{-3}$)	0.5	0	0
Equilibrium concentration ($mol\,dm^{-3}$)	$0.5 - x$	x	x

We can now write the relationship between these concentrations and K_a:

$$K_a = \frac{[H^+(aq)][A^-(aq)]}{[HA(aq)]}$$

$$= \frac{x \times x}{0.5 - x}$$

Now the value of x is small for this acid because it is only weakly ionised, so we can assume that x is very small compared to $0.5\,mol\,dm^{-3}$, and can write:

$$K_a = \frac{x\,mol\,dm^{-3} \times x\,mol\,dm^{-3}}{0.5\,mol\,dm^{-3}}$$

Substituting for K_a:

$$1.6 \times 10^{-4}\,mol\,dm^{-3} = \frac{(x\,mol\,dm^{-3})^2}{0.5\,mol\,dm^{-3}}$$

Rearranging this gives:

$$(x\,mol\,dm^{-3})^2 = 1.6 \times 10^{-4}\,mol\,dm^{-3} \times 0.5\,mol\,dm^{-3}$$

$$x = \sqrt{1.6 \times 10^{-4}\,mol\,dm^{-3} \times 0.5\,mol\,dm^{-3}}$$

$$= 8.9 \times 10^{-3}\,mol\,dm^{-3}$$

Now this is the value of $[H^+(aq)]$. The pH can be found from:

$$pH = -\log[H^+(aq)]$$

$$= -\log(8.9 \times 10^{-3})$$

$$= 2.05$$

Strong base

To find the pH of a solution of a base, we must **first find the concentration of OH^- ions**, and then **use the ionic product of water, K_w, to find the concentration of H^+ ions**.

We can assume that, like a strong acid, a **strong base is completely ionised in aqueous solution**. This will be true whether the base produces OH^- ions directly as it dissolves in water or they are produced as a result of the reaction of the base with water.

Weak base

Calculating the pH of a solution of a weak base requires the use of K_b – the method is very similar to that used with K_a to find the pH of a solution of a weak acid.

	$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$		
Initial concentration ($mol\,dm^{-3}$)	0.1	0	0
Equilibrium concentration ($mol\,dm^{-3}$)	$0.1 - x$	x	x

We can now write down the relationship between these concentrations and K_b:

$$K_b = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$$

$$= \frac{x^2}{(0.1 - x)\,mol\,dm^{-3}}$$

Now the value of K_b is small because ammonia is a weak base, so we can assume that x is much smaller than $0.1\,mol\,dm^{-3}$, and we can write:

$$K_b = \frac{x^2}{0.1\,mol\,dm^{-3}}$$

Substituting for K_b:

$$1.8 \times 10^{-5}\,mol\,dm^{-3} = \frac{x^2}{0.1\,mol\,dm^{-3}}$$

Rearranging this gives:

$$x^2 = 1.8 \times 10^{-5}\,mol\,dm^{-3} \times 0.1\,mol\,dm^{-3}$$

$$x = \sqrt{1.8 \times 10^{-5}\,mol\,dm^{-3} \times 0.1\,mol\,dm^{-3}}$$

$$= 1.34 \times 10^{-3}\,mol\,dm^{-3}$$

This is the value of the hydroxide ion concentration, $[OH^-(aq)]$. But:

$$[H^+(aq)][OH^-(aq)] = 1.0 \times 10^{-14}\,mol^2\,dm^{-6}$$

$$[H^+(aq)] = \frac{1.0 \times 10^{-14}\,mol^2\,dm^{-6}}{1.34 \times 10^{-3}\,mol\,dm^{-3}}$$

$$= 7.46 \times 10^{-12}\ mol\,dm^{-3}$$

The pH can be found from:

$$pH = -\log[H^+(aq)]$$

$$= -\log(7.46 \times 10^{-12})$$

$$= 11.12$$

6 Determination of K_A for a weak acid

Method

A small quantity of the acid is weighed out and dissolved in a small amount of water. It is not a very soluble substance and warm water could be used and the solution allowed to cool. It is then diluted with water in a volumetric flask to make up a standard solution.

We know the mass of the acid used, the volume of the solution, and the molar mass of the acid, so we will be able to work out the concentration of the acid in mol dm^{-3}.

Next, we ensure that the solution is mixed completely and take a sample of it. We measure its pH using a calibrated pH meter.

We know that pH = - log[H^+(aq)], so we can work out the hydrogen ion concentration.

The value of K_a can then be found using the equilibrium expression for that reaction.

Assumption and evaluation

- It is assumed that no dissociation takes place.
- It is assumed that the reactants are pure and pure deionised water was used.
- Small amount of acid is used so a sophisticated balance should be used to decrease the percentage uncertainty in the measurement.
- A volumetric flask enables a standard solution to be prepared accurately, but the solution must be mixed thoroughly.
- The method of measuring the pH of the acidic solution is clearly important. Even slight differences in pH make a considerable difference to the value of K_a obtained. If only coloured indicators were available, then it would be very difficult to get an accurate and reliable result. With a correctly calibrated pH meter more accurate results are obtainable.

7 Dilution effects

- Strong acids are already fully dissociated into ions in dilute aqueous solutions, so [H^+(aq)] = [acid], the acid concentration in mol dm^{-3}.
- Diluting a strong acid by a factor of 10 raises the pH by 1 unit.
- For an acid like hydrochloric acid:

Concentration/ mol dm^{-3}	0.1	0.01	0.001
pH	1	2	3

- Diluting a weak acid is different; it increases the degree of dissociation into ions.

8 pH CHANGES DURING ACID-BASE TITRATIONS

It might be expected that there will be a gradual change in pH as you add a dilute acid solution to a dilute alkali solution – but this is not so. The shape of the graph of pH against volume of acid added depends on whether the acid and base involved are strong or weak.

When you carry out a simple acid-base titration, you usually use an indicator to show when the acid and alkali are mixed exactly the right proportions to neutralise each other.

- The end-point of the titration is when the appropriate colour change takes place. The end-point can be determined using indicators or by using a pH meter or pH paper.
- The equivalence point is when the two reactants are mixed in exactly the proportions indicated by the equation. Sometimes, this might also correspond to the neutral point as well.

A titration curve may be drawn to determine the end-point of a titration as well as illustrating the equivalence point. **A titration curve is a plot of measured pH against volume of acid added or vice versa.** The end-point is halfway up the vertical section of the pH curve, where the pH changes most rapidly. There is no sharp change of pH with weak acid-weak base titrations, making it very hard to determine the end-point.

Note that:

- Only the titrations of strong acids with strong bases give end-points with pH 7.
- Neutralisation of a weak acid or weak base moves the end-point above or below 7 respectively.

Titration curves

It is possible to draw titration curves for monobasic acids. Monobasic acids have one replaceable hydrogen atom.

Titration of a strong acid and a strong base

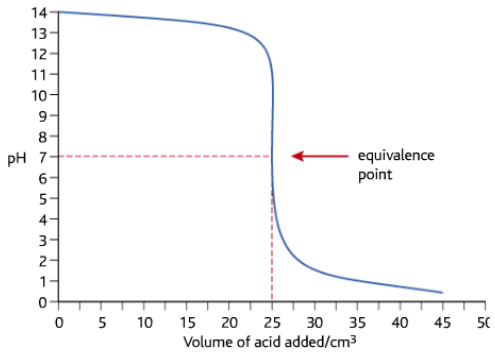


fig. 1.5.11 Change in pH for strong acid–strong base titration.

Titration of a weak acid and a strong base

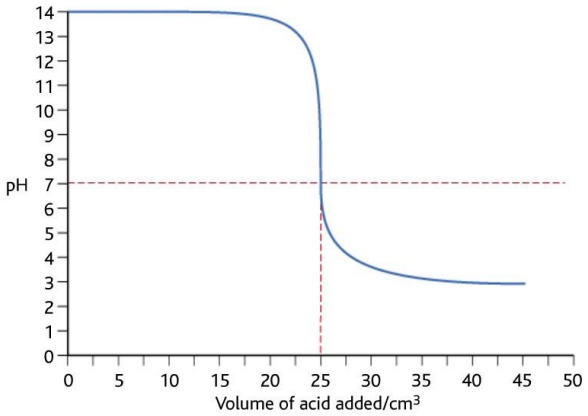


fig. 1.5.12 Change in pH for weak acid–strong base titration.

Titration of a strong acid and a weak base

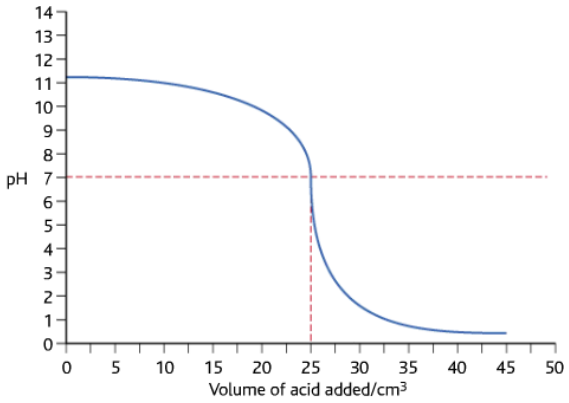


fig. 1.5.13 Change in pH for strong acid–weak base titration.

Titration of a weak acid with a weak base

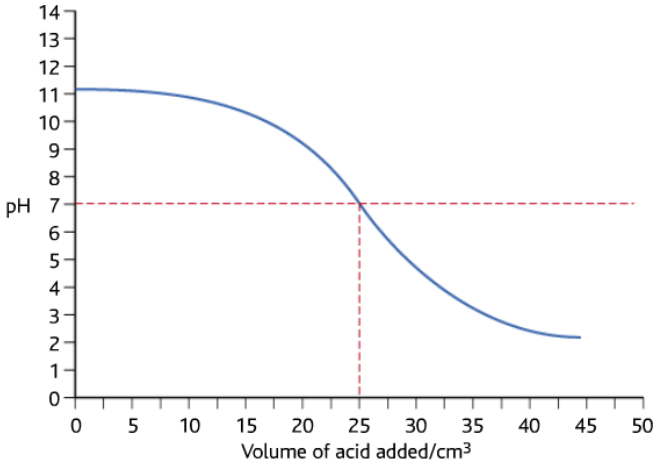


fig. 1.5.14 Change in pH for weak acid–weak base titration.

9 FINDING K_A FOR A WEAK ACID FROM A pH TITRATION

It is possible to find the K_a of an acid as if half of an acid is neutralised then:

pK_a = pH

The titration method can be used to calculate K_a for a weak acid.

Method 1

This experiment involves carrying out a titration starting with weak acid in a conical flask and a standard solution of sodium hydroxide in the burette. You measure the pH of the solution after each addition of the acid, and plot a graph of pH against volume of hydroxide solution.

From the titration curve drawn it is possible to find the volume of sodium hydroxide needed to neutralise the acid – the equivalence point. You can then find the half-equivalence point and estimate the pH at that point.

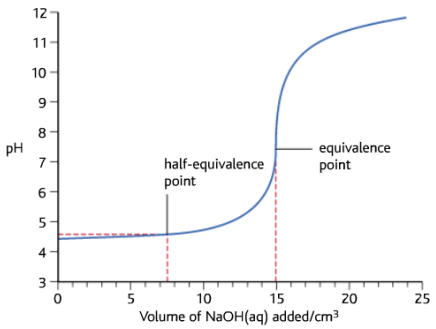


fig. 1.5.17 Titration curve and the half-equivalence point.

Method 2

This is sometimes called the half volume method because it involves titrating until half of the molecules of the weak acid have reacted. The concentrations of weak acid molecules and its conjugate base ions are then equal.

A standard solution of known concentration of the weak acid is prepared and two portions of equal volume are measured. The first portion is titrated with standard sodium hydroxide solution using phenolphthalein as indicator.

You stop adding acid when the solution just goes pink and stays pink – this is the end-point. Now you add the second portion of the standard weak acid solution and mix thoroughly. The pH of the solution is measured using a calibrated pH meter. This solution now has equal concentrations of weak acid molecules and conjugate base ions. The value of K_a is calculated.

10 CHOOSING SUITABLE INDICATORS

Acid-base indicators are generally weak acids or weak bases. For an indicator that is a weak acid, the dissociation into ions can be represented as:

$$HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$$

Either the weak acid or its conjugate base is coloured. If the pH increases the equilibrium moves to the right to produce more In^-, which causes a change in colour. For example, the indicator phenolphthalein is colourless in its protonated form and pink in its unprotonated form. Below a pH of 9, phenolphthalein is colourless. Adding hydroxide ions removes protons from the right-hand side of the equilibrium, pulling it to the right. This causes more of the unprotonated form of the indicator to be produced, and causes the solution to turn pink.

Indicators and end-points

The end-point of a titration occurs when the two solutions have reacted exactly. The ideal indicator for a given acid-base titration is one that is in the **middle of its colour change at the pH of the equivalence point of the titration**. This pH depends on the acid and base being titrated.

The reason for this can be understood if we think carefully about the equilibrium constant for the dissociation of the indicator, K_{in}, given by:

$$K_{in} = \frac{[H^u(aq)][In^-(aq)]}{[HIn(aq)]}$$

In the middle of colour change of the indicator, the two forms of the indicator, HIn and In^-, are present in equal amounts, so $[HIn(aq)] = [In^-(aq)]$. The expression above then simplifies to:

$$K_{in} = [H^+(aq)]$$
$$\text{or } pK_{in} = pH$$

In other words, pK_{in} for an indicator should be equal or close as possible to the pH of the equivalence point of the titration.

Indicator	Colour change	pH range of use
Methyl orange	Red–yellow	3.2–4.4
Methyl red	Red–yellow	4.8–6.0
Bromothymol blue	Yellow–blue	6.0–7.6
Phenol red	Yellow–red	6.8–8.4
Phenolphthalein	Colourless–pink	8.3–10.0

Choosing an indicator for a titration

A good indicator must show a dramatic colour change in order to make it easy to detect the end-point of a titration. At the equivalence point of a titration, the pH must change sharply by several units if the end-point is to coincide with the equivalence point. The pH change during a titration is greatly dependent on the acid and base being titrated, and indicators must be selected accordingly. The vertical portion of the corresponding titration curve should be considered.

11 BUFFER SOLUTIONS

Natural systems have mechanisms that help to prevent large changes in pH happening, and chemists have developed ways of stabilising the pH of solution in which reactions are occurring. Natural and artificial solutions that contain solutes which together resist changes in pH are known as buffer solutions – they are said to be buffered against changes in the pH.

The principles of buffer solutions can be understood using the ideas of equilibria. A buffer solution usually consists of two solutes dissolved in water. One of these is a weak acid and the other is its conjugate base – in other words, a weak acid and one of its salts.

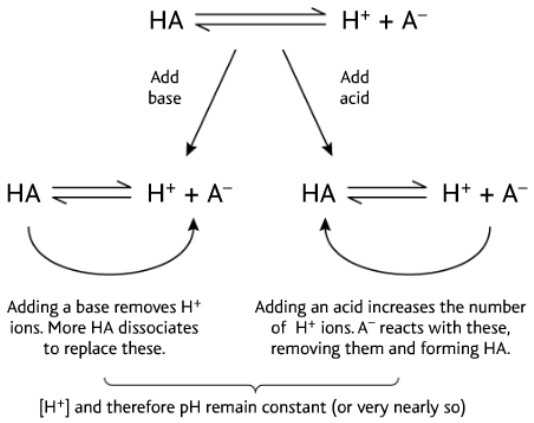
If we represent the weak acid as HA, the equilibrium concerned can be written:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

If we represent the salt as MA, this will be fully dissociated:

$MA(s) \rightarrow M^+(aq) + A^-(aq)$

From these two equations, you can see that the buffer solution contains large amount of A^-. This pushes the acid-base equilibrium to the left, so the solution also contains a large amount of HA. The solution thus has a reservoir of the weak acid and a reservoir of its conjugate base. This prevents changes in the pH. However, the pH value will change if a large excess of acid or base is added.


HA ⇌ H⁺ + A⁻
Add base
Add acid
HA ⇌ H⁺ + A⁻
HA ⇌ H⁺ + A⁻
Adding a base removes H⁺ ions. More HA dissociates to replace these.
Adding an acid increases the number of H⁺ ions. A⁻ reacts with these, removing them and forming HA.
[H⁺] and therefore pH remain constant (or very nearly so)

As the diagram shows, the stability of the pH of a buffer solution is due to two factors:

- A reservoir of HA, which supplies H^+ ions if they are removed from the solution.
- A reservoir of A^-, which reacts with any H^+ ions added removing them from the solution.

➔ A buffer solution consisting of a weak acid and one of its salts is an acidic buffer solution, with a pH below 7.

➔ A buffer solution above pH 7 – an alkaline buffer solution – can be made by mixing a weak base and one of its salts.

12 pH OF BUFFER SOLUTIONS

Consider a buffer solution made by dissolving a salt, MA, in solution of a weak acid, HA. We know that the dissociation constant of the acid, K_a is given by:

$$K_a = \frac{[H^+(aq)][A^-(aq)]}{[HA(aq)]}$$

This relationship can be rearranged so that $[H^+(aq)]$ is on the left-hand side of the equation:

$$[H^+(aq)] = K_a \times \frac{[HA(aq)]}{[A^-(aq)]}$$

Strictly speaking the concentrations appearing in this expression are equilibrium concentrations. However, we are dealing with a solution of a weak acid plus a large reservoir of its conjugate base. Because of this, the equilibrium:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

will lie well to the left-hand side, and the acid will be hardly dissociated at all. The concentration of the acid at equilibrium will, therefore, effectively be equal to the initial concentration of the acid. In the same way, the concentration of the ion A^- will effectively be the concentration supplied by the salt. We can represent these simplifying assumptions as:

$$[HA(aq)]_{eq} \approx [HA(aq)]_{initial} = [acid]$$
$$[A^-(aq)]_{eq} \approx [A^-(aq)]_{initial} = [base]$$

Substituting these simplifications into the equation above:

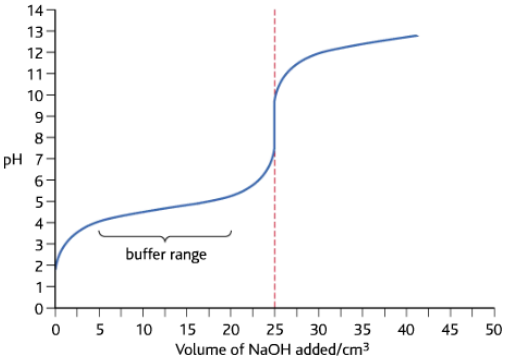
$$-[H^+(aq)] = -K_a \times \frac{[acid]}{[base]}$$
$$-\log[H^+] = -\log K_a - \log \frac{[acid]}{[base]}$$
$$pH = pK_a - \log \frac{[acid]}{[base]}$$

Note that $\frac{[acid]}{[base]}$ is the ratio of the acid to the base. So, the pH of a buffer solution depends on this ratio and it will be affected very little by dilution – because diluting it will decrease both concentrations by a similar amount. It will also be useful to realise that when $[acid] = [base]$ then the relationship simplifies to:

$$[H^+(aq)] = K_a$$
$$\text{or } pH = pK_a$$

13 pH OF BUFFER SOLUTIONS

The diagram shows part of the pH curve when titrating a weak acid with a strong base. In the portion marked buffer range, the change in pH as sodium hydroxide is added is gradual. Over this range, there are significant concentrations of weak acid molecules and conjugate base ions – and so there is buffer action.



14 BUFFERS IN BIOLOGICAL SYSTEMS

Buffers in the body

The human body operates within a narrow range of pH values. Oxygen is carried in the blood bound to haemoglobin. The key equilibrium for this process is:

$$HHb(aq) + O_2(g) \rightleftharpoons H^+(aq) + HbO_2^-(aq)$$

The presence of H^+ on the right-hand side of the equilibrium means that the equilibrium position is very sensitive to the hydrogen ion concentration in the fluid.

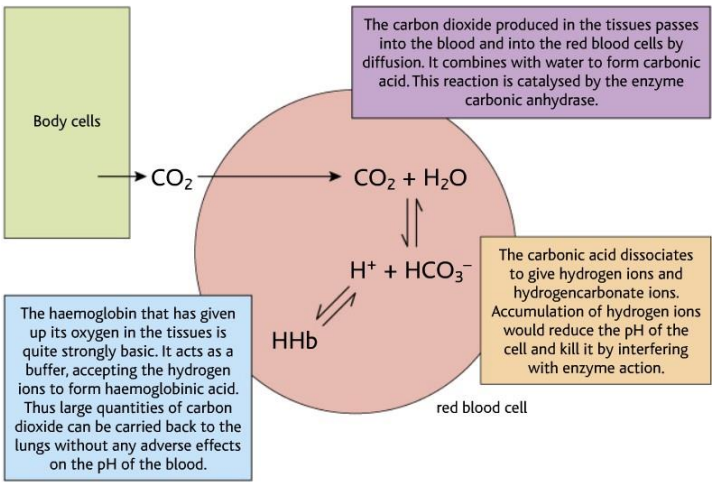

Body cells
CO2
CO2 + H2O
H+ + HCO3−
HHb
The carbon dioxide produced in the tissues passes into the blood and into the red blood cells by diffusion. It combines with water to form carbonic acid. This reaction is catalysed by the enzyme carbonic anhydrase.
The carbonic acid dissociates to give hydrogen ions and hydrogencarbonate ions. Accumulation of hydrogen ions would reduce the pH of the cell and kill it by interfering with enzyme action.
The haemoglobin that has given up its oxygen in the tissues is quite strongly basic. It acts as a buffer, accepting the hydrogen ions to form haemoglobinic acid. Thus large quantities of carbon dioxide can be carried back to the lungs without any adverse effects on the pH of the blood.
red blood cell

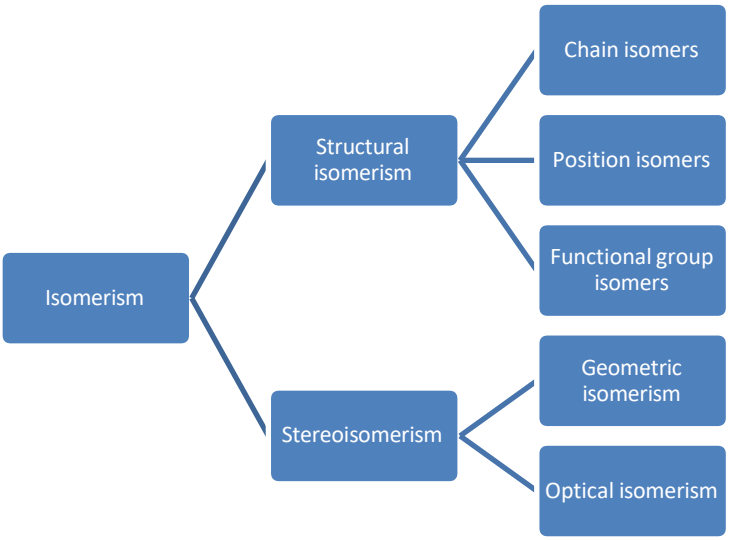
fig. 1.5.24 The pH of the blood is controlled in part through the buffering effect of haemoglobin.

Buffers in food

Spoilage of food by microorganisms depends greatly on the pH value of the food. Most microorganisms thrive when the pH of their surroundings is approximately neutral. The metabolism of these microorganisms is then greatest and they can multiply fast. Therefore, many processed foods contain buffer systems which help to maintain the pH within a range where the growth of microorganisms is very slow or non-existent.

Further organic chemistry

1 Chirality



1 ISOMERISM AND CHIRALITY

Stereoisomerism

Stereoisomerism is when two or more compound with the same molecular formula have a three dimensional arrangement of the bonds which allows different orientations in space so the molecules cannot be superimposed on each other.

- Geometric isomerism

It is a chemical compound which has the same molecular formula as another but a different geometric configuration because atoms or groups of atoms are attached on either side of a double bond or other rigid bond. It arises due to the lack of free rotation of groups around a bond.

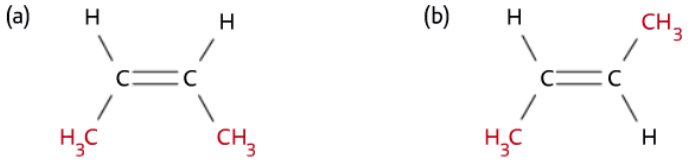


fig. 1.6.2 Geometric isomers of but-2-ene: (a) *cis*-but-2-ene (*Z*); (b) *trans*-but-2-ene (*E*).

- Optical isomerism

They are molecules with the same molecular formula and groups of atoms but with different spatial arrangements such that they are non-superimposable mirror images of each other. These molecules are also said to be chiral. The simplest type of chiral molecule is where four different groups are attached to one carbon atom, which acts as a chiral centre. This carbon atom is sometimes called an asymmetric carbon atom and indicated with an asterisk.

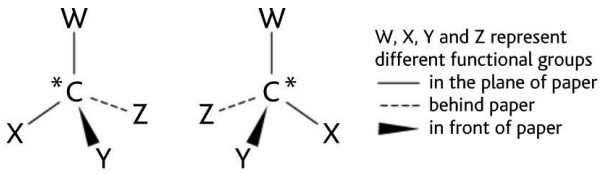


fig. 1.6.3 Representing three-dimensional molecules in two dimensions.

Isomers that are mirror images of each other are called enantiomers. They are remarkably similar in both their physical and chemical properties. Unlike structural and geometric isomers, they cannot be told apart by differences in their physical properties or chemical reactivities. However, they do have one difference which allows us to identify them – they have different effects on plane-polarised light. Compounds such as these are said to be optically active and their isomers are known as optical isomers.

2 OPTICAL ACTIVITY

Optical activity is the ability of a single optical isomer to rotate the plane of polarisation of plane-polarised monochromatic light in molecules containing a single chiral centre.

Rotation of plane-polarised light

The wave model envisages light as a form of electromagnetic radiation travelling as a transverse wave. This means that the direction in which disturbance takes place is at right angles to the direction in which the wave travels. A light beam that, passes through a piece of Polaroid, leaves with all the waves vibrating in the same plane. If a transparent sample containing a single enantiomer is placed in front of a Polaroid, then it will rotate the plane of the light because it is optically active. You would then have to rotate a second piece of

Polaroid through an angle, called the angle of rotation, to return to the situation where no light passes through.

The rotation may be clockwise (+) or anticlockwise (-). This principle is used in the polarimeter. The optical activity of a substance is measured in terms of number of degrees by which plane-polarised light is rotated as it passes though a solution of a substance. **One optical isomer rotates the plane of polarisation of light in clockwise direction and the other one in anticlockwise direction.**

Therefore, it is worth noting that some solutions of optically active substances have no effect on plane-polarised light. This happens when a racemic mixture is present.

Racemic mixture: An equal mixture of two optical isomers resulting in no overall rotation of plane-polarised light.

The clockwise rotation caused by one enantiomer is balanced by the anticlockwise rotation caused by the other.

3 OPTICAL ACTIVITY AND EVIDENCE FOR REACTION MECHANISMS

The S_N2 mechanism

We are going to consider the nucleophilic substitution reaction of an enantiomer that rotates the plane of plane-polarised light clockwise (+). This is summarised in **fig. 1.6.12**.

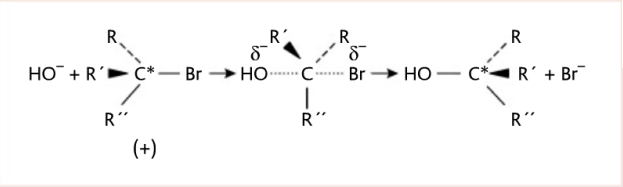


fig. 1.6.12 Nucleophilic substitution by the S_N2 mechanism.

The arrangement of the three groups R, R' and R'' attached to the chiral carbon atom is effectively turned inside out during the reaction. This is called **inversion** of the configuration. If the product could be a bromide rather than an alcohol, we know that rotation of plane-polarised light would be in the opposite direction (i.e. –). Since the product is an alcohol, we cannot tell merely by observing the direction of optical rotation whether it has the same or the opposite configuration to the bromoalkane from which it is derived. Other than mirror images, compounds having opposite configurations do not necessarily cause opposite directions of optical rotation, any more than do compounds of the same configuration necessarily cause the same direction of optical rotation.

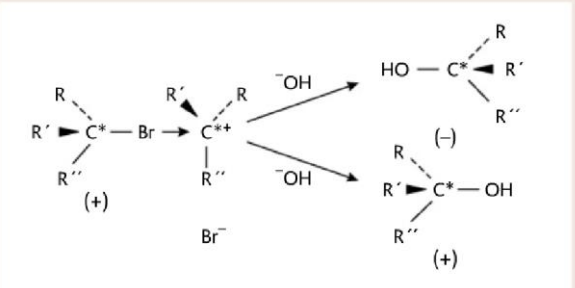
Further studies have shown that inversion of the configuration occurs when an S_N2 reaction occurs.

The S_N1 mechanism

We are going to consider again the case where the reactant molecule is an enantiomer which rotates plane-polarised light clockwise (+).

You may remember that in this mechanism the first step, the slow rate-determining step, involves the loss of the halogen as a halide ion and the formation of a carbocation. The carbocation is planar.

We might expect that the attacking nucleophile, e.g. OH^-, can attack the carbocation from either the front or the back, and so the product is likely to contain a 1:1 mixture of the two enantiomers of the alcohol product. Hence, we would expect the product to be a racemic mixture and the product to be optically inactive. This is shown in **fig. 1.6.13**.



In practice, the product often shows complete, or virtually complete, formation of the racemic mixture but it depends how rapidly the nucleophile attacks the central carbon atom of the carbocation. If the solvent can also act as a nucleophile (e.g. H_2O) then attack is likely to be more rapid even before the carbocation can achieve its planar form. The result will be more inversion.

2 Carbonyl compounds

1 THE NATURE OF CARBONYL COMPOUNDS

There are two types of carbonyl compounds known as the aldehydes and ketones.

In aldehydes, the **carbonyl carbon has a hydrogen atom attached to it**, together with either a second hydrogen atom, or, much more commonly a hydrocarbon group, which might be an alkyl group or one containing a benzene ring. Aldehydes can be produced by the oxidation of primary alcohols.

In ketones, the **carbonyl group has two hydrocarbon groups** attached. Again these can be either alkyl groups or groups containing benzene rings. Ketones can be produced by the oxidation of secondary alcohols.

fig. 1.6.20 The general formulae of aldehydes and ketones.

The carbonyl group

There is a σ-bond and a π-bond in a carbonyl group. Oxygen has a much higher electronegativity than carbon, so the electrons in the double bond are attracted more towards the oxygen atom – this is especially true of the π-bond. The bond is permanently polarised and the result is a {+ charge on the carbon atom and a {- on the oxygen atom. As a result, the **electron density is not equally distributed** and this affects both the physical and chemical properties of aldehydes and ketones.

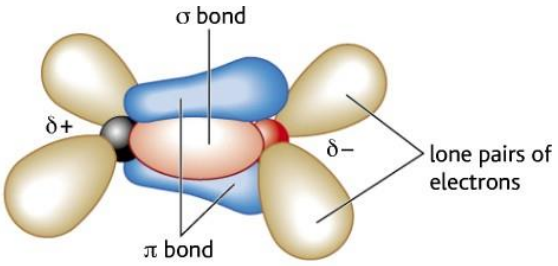
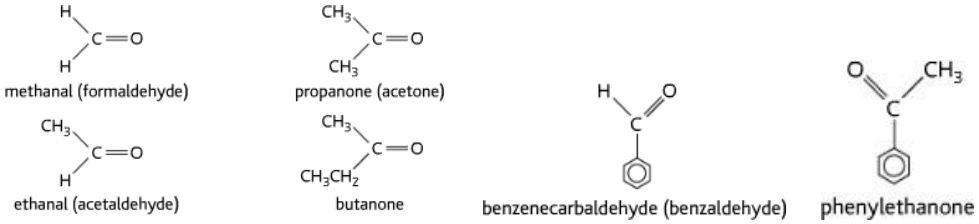


fig. 1.6.18 The pair of electrons in a carbonyl group spend more time around the more electronegative oxygen atom, shown here in red.

Examples for carbonyl compounds



2 PHYSICAL PROPERTIES OF ALDEHYDES AND KETONES

The physical properties of the aldehydes and ketones are largely influenced by the presence of the carbonyl group. This influence is particularly marked in compounds with molecules of relatively short-length carbon chains – as the chains get longer they have an increasing effect on the chemistry of compounds.

The carbonyl group cannot take part in hydrogen bonding, but there are permanent dipole-dipole interactions between aldehyde molecules and between ketone molecules. This gives them boiling temperatures which are higher than those of the corresponding alkanes, but lower than those of the corresponding alcohols.

A further point about the boiling temperatures of the aldehydes and ketones is that molecules of straight-chain isomers can pack closer together than those of branched-chain molecules. This means that the forces between molecules of straight-chain isomers are stronger than those between molecules of branched-chain isomers – so the boiling temperatures of straight-chain isomers are higher.

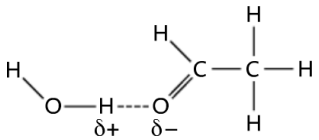
Both the families of carbonyl compounds have members with strong odours, but the aldehydes are particularly responsible for imparting characteristic smells and flavours to a variety of foods.

Solubility of aldehydes and ketones in water

Aldehydes and ketones composed of small molecules are miscible with water in all proportions, but this decreases with increasing chain length.

The reason for the solubility is that they can form hydrogen bonds with water molecules even though they cannot form hydrogen bonds with themselves. With its {+ charge, one of

the water molecule's hydrogen atoms can be sufficiently attracted to one of the lone pairs on the oxygen atom of a carbonyl group for a hydrogen bond to be formed.



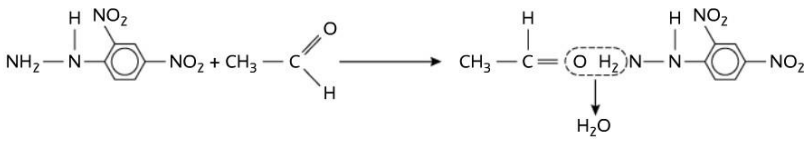
Dispersion forces and dipole-dipole attractions between the aldehyde or ketone and the water molecules will also exist. Forming these attractions releases energy, which helps to supply the energy needed to separate the water molecules and aldehyde or ketone molecules from each other so that they can mix together.

As chain length increases, the hydrocarbon portions of the molecules prevent such attractions occurring.

3 THE REACTIONS OF CARBONYL COMPOUNDS

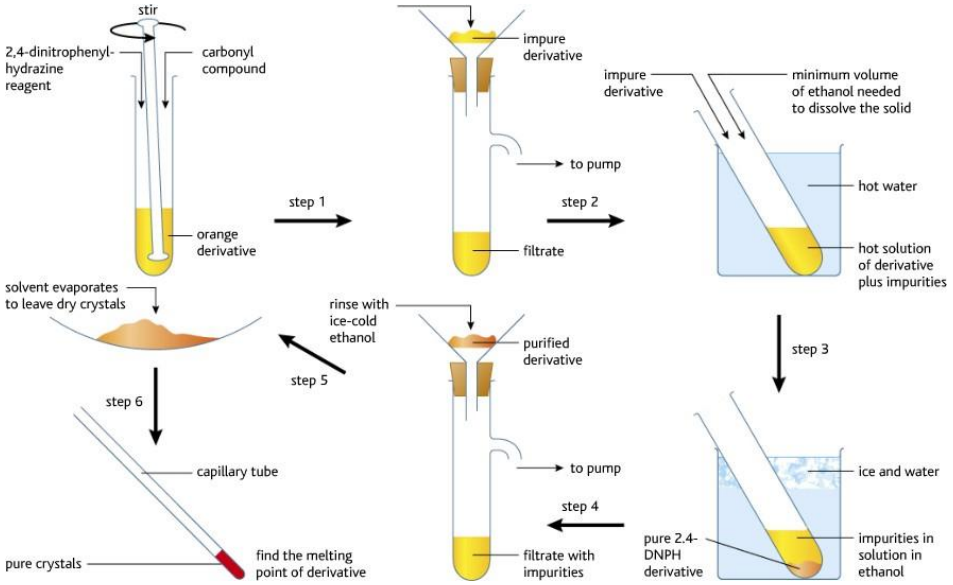
1-) Brady's reagent

2,4-dinitrphenylhydrazine is a red-orange solid, usually supplied wet to reduce the risk of explosion. Aldehydes and ketones react with Brady's reagent to form yellow/orange/red crystalline solids. These solids are called 2,4-dinitrphenylhydrazine derivatives. They have no practical use other than in identifying aldehydes and ketones.



2,4-dinitrophenylhydrazine ethanal ethanal 2,4-dinitrophenylhydrazone

The reaction that takes place is a condensation reaction – this involves addition followed by the elimination of water. The derivative can be removed by filtration and purified by recrystallisation. These compounds have characteristic melting temperatures which can be compared with values given in data books.



2-) Oxidation reactions of aldehydes

Aldehydes and ketones can be distinguished by their oxidation reactions. Aldehydes have a hydrogen atom that forms part of the functional group. This hydrogen is activated by the carbonyl group and, as a result, aldehydes are readily oxidised to carboxylic acids by even quite mild oxidising agents. In contrast, ketones have no such hydrogen atom and so they are very resistant to oxidation – they only react after prolonged treatment with a very strong oxidation agent.

- Acidified dichromate (VI) ions

The oxidation of aldehydes can be carried out by warming with a solution of potassium dichromate(VI) acidified with sulfuric acid. For example:

$$\underset{\text{ethanal}}{3CH_3CHO(l)} + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow \underset{\text{ethanoic acid}}{3CH_3COOH(aq)} + 4H_2O(l) + 2Cr^{3+}(aq)$$

- Fehling's and Benedict's solution

This contains an aqueous alkaline solution containing Cu^{2+} ions. Normally these would give a precipitate of copper (II) hydroxide under these conditions, but in Fehling's solution the copper(II) ions are prevented from precipitating by complexing them with 2,3-dihydroxybutanedioate ions.

If an aldehyde is warmed with Fehling's solution then the aldehyde is oxidised to a carboxylic acid, and the Fehling's solution is reduced, giving a red-brown precipitate of copper(I) oxide. The half equations are:

$$2Cu^{2+}(aq) + OH^{-}(aq) + 2e^{-} \rightarrow Cu_2O(s) + H^{+}(aq)$$

$$RCHO(aq) + H_2O(l) \rightarrow RCOOH(aq) + 2H^{+}(aq) + 2e^{-}$$

so overall:

$$2Cu^{2+}(aq) + RCHO(aq) + OH^{-}(aq) + H_2O(l) \rightarrow Cu_2O(s) + RCOOH(aq) + 3H^{+}(aq)$$

If a ketone is warmed with Fehling's solution in the same way then there is no reaction.

Colour change with aldehyde: blue → red

Benedict's solution gives the same result. Both Benedict's and Fehling's solution give a positive test with reducing sugars and some aldehydes. Both consist of a solution of copper(II) ions in alkaline solution but they use different chemicals to prevent the copper(II) hydroxide precipitating.

- Tollens' reagent

This is produced by dissolving silver nitrate in water and adding aqueous ammonia. Silver(I) oxide is formed as a precipitate initially but this dissolves as more ammonia is added forming a complex – the diamminesilver(I) ion, $[Ag(NH_3)_2]$. When Tollens' reagent is warmed gently with an aldehyde, the aldehyde is oxidised and the silver(I) ions in the complex are reduced to form silver metal. With careful preparation, this coats the inside of the test tube as a silver mirror – or less successfully as a black precipitate.

The half reactions are:

$$2Ag^{+}(aq) + 2e^{-} \rightarrow 2Ag(s)$$

$$RCHO(aq) + H_2O(l) \rightarrow RCOOH(aq) + 2H^{+}(aq) + 2e^{-}$$

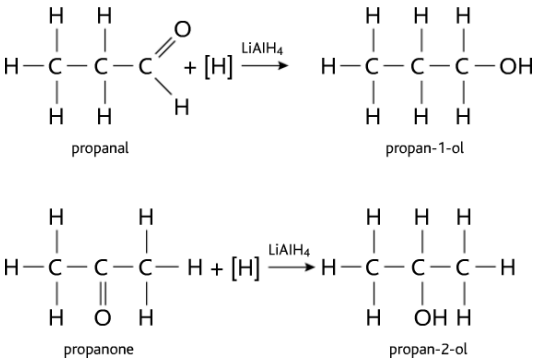
so overall:

$$2Ag^{+}(aq) + RCHO(aq) + H_2O(l) \rightarrow 2Ag(s) + RCOOH(aq) + 2H^{+}(aq)$$

If a ketone is warmed with the same reagent, there is no reaction.

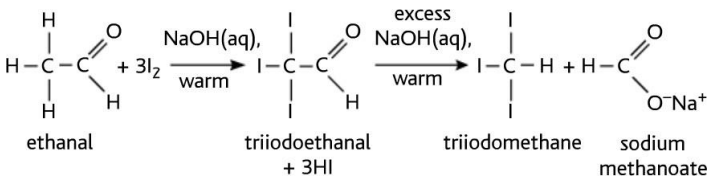
3-) Reduction reactions of aldehydes and ketones

Partial oxidation of a primary alcohol produces an aldehyde, and oxidation of a secondary alcohol produces a ketone. These reactions can be reversed by reduction – so aldehydes are readily reduced to primary alcohols, and ketones to secondary alcohols. Suitable reagents include **tetrahydridoaluminate ($LiAlH_4$) dissolved in dry ether (ethoxyethane)**.



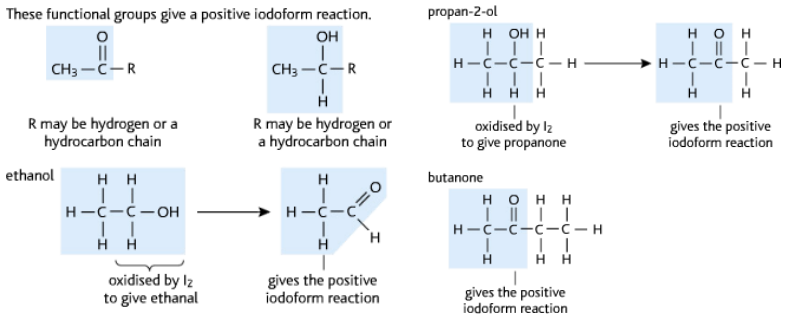
4-) The triiodomethane reaction

When ethanal is warmed with iodine in alkaline solution, a two-stage reaction takes place.



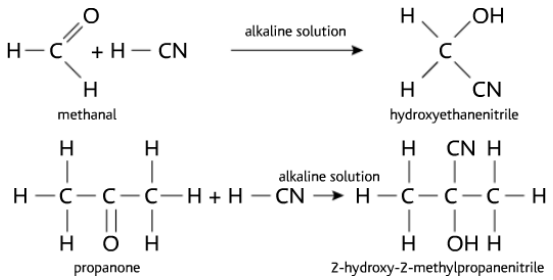
First, the aldehyde reacts with the iodine to form triiodoethanal; and then this reacts with the alkali to form triiodomethane. Triiodomethane (or iodoform) is an insoluble yellow solid with a characteristic smell. It forms a precipitate.

This iodoform reaction is specific to organic compounds that contain a methyl group next to a carbonyl group or can react to give a methyl group next to a carbonyl group.


These functional groups give a positive iodoform reaction.
R may be hydrogen or a hydrocarbon chain
R may be hydrogen or a hydrocarbon chain
propan-2-ol
oxidised by I2 to give propanone
gives the positive iodoform reaction
ethanol
oxidised by I2 to give ethanal
gives the positive iodoform reaction
butanone
gives the positive iodoform reaction

5-) Addition reactions with hydrogen cyanide

Aldehydes and ketones undergo an addition reaction with hydrogen cyanide to produce hydroxynitriles. The HCN molecule adds across the C=O bond.

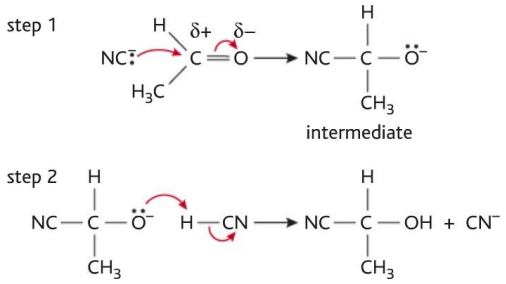


This happens in presence of potassium cyanide in cold, alkaline solution. In aqueous solution, the acid-base equilibrium:

$$K^+(aq) + CN^-(aq) + H_2O(l) \rightleftharpoons K^+(aq) + HCN(aq) + OH^-(aq)$$

is established. On the left-hand side of this equilibrium is a species of CN^-, which is a weak Brønsted base. On the right-hand side is the OH^- ion, which is a much stronger base than CN^-. The net result is that the hydroxide ion competes more effectively for the proton than the cyanide ion, and the reaction is pushed to left, forming CN^-. This is the nucleophile needed for attacking the carbon atom on the carbonyl group.

In the first step, the incoming nucleophile CN^-, has a lone pair of electrons. It attacks the central carbon atom, displacing a pair of electrons in the double bond and pushing them onto the oxygen atom. The oxygen then has a negative charge.



Finally, in the second, fast, step the negatively charged oxygen acts as a base and gains a proton to make the final product.

Stereochemistry of the reaction

When hydrogen cyanide reacts with ethanal to form a hydroxynitrile, the molecule formed contains an asymmetrical carbon atom, and is therefore optically active. Despite this, the products of the reaction show no optical activity. The reaction produces equal quantities of the two optical isomers of the hydroxynitrile, which rotate the plane of plane-polarised light in opposite directions. Each isomer cancels out the effect of the other, so no overall rotation of the plane of polarisation is seen.

3 Carboxylic acids

1 THE PROPERTIES OF CARBOXYLIC ACIDS

Carboxylic acids contain the carboxyl group. This is a complex functional group which is made up of a hydroxyl group –OH and a carbonyl group C=O. These two functional groups are so close together they affect each other. Because of this, the reactions of the carboxylic acids tend to differ from those of the corresponding alcohols, aldehydes and ketones.

The properties of the carboxylic acids, both physical and chemical, are largely governed by two factors:

- The polarity of the carboxyl group
- The length of the carbon chain

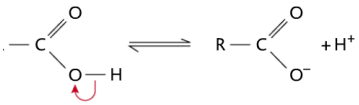
Physical properties of carboxylic acids

The presence of two polarised groups means that carboxylic acid molecules experience relatively strong intermolecular forces. So they have relatively high melting and boiling temperatures. Furthermore, the polarity and structure of the molecules is such that they can exist as hydrogen-bonded dimmers in all states.

Hydrogen bonding is also responsible for the high solubility of the smaller carboxylic acid molecules in water and other polar solvents. Longer-chained acids become less soluble because the organic nature of the carbon chain becomes dominant.

Acidic properties of carboxylic acids

When a carboxylic acid is dissolved in water, it dissociates forming hydrogen ions and carboxylate ions, so behaving as an acid. Although the carboxylate ion is drawn with one double bond, X-ray diffraction analysis and observations of the ways in which it reacts suggest that the two carbon-oxygen bonds are actually identical. This implies that the negative charge is delocalised over the whole of the carboxylate group, which means that it will not attract positively charged particles as strongly as might be expected. The carboxylic acids are relatively strong acids and the carboxylate ion is a relatively weak base.



g. 1.6.42 The dissociation of a carboxylic acid.

2 PREPARATION OF CARBOXYLIC ACIDS

Carboxylic acids can be prepared by the following methods.

- Prolonged oxidation of primary alcohols or aldehydes

$$\underset{\text{ethanol}}{CH_3CH_2OH(l)} + 2[O] \rightarrow \underset{\text{ethanoic acid}}{CH_3COOH(aq)} + H_2O(l)$$

- Hydrolysis of a nitrile by boiling with a dilute acid

$$\underset{\text{propanenitrile}}{CH_3CH_2CN(l)} + 2H_2O(l) + H^+(aq) \rightarrow \underset{\text{propanoic acid}}{CH_3CH_2COOH(aq)} + NH_4^+(aq)$$

3 THE REACTIONS OF CARBOXYLIC ACIDS

1-) Reduction

Carboxylic acids are not easy to reduce and reduction is only possible back to the alcohol and no the aldehyde. A suitable reducing agent is lithium tetrahydridoaluminate suspended in dry ether (ethoxyethane) at room temperature.

$$CH_3CH_2COOH(l) + 2[H] \rightarrow CH_3CH_2CH_2OH(l) + H_2O(l)$$

Addition of water at the end of the reaction will destroy any excess lithium tetrahydridoaluminate.

2-) Neutralisation

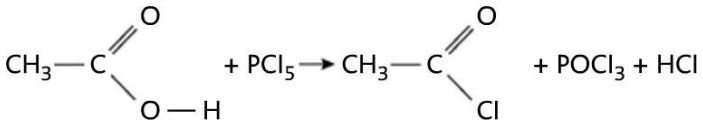
Like any acid, carboxylic acids will react with a base to form a salt and water.

$$CH_3COOH(aq) + NaOH(aq) \rightleftharpoons CH_3COO^-(aq) + Na^+(aq) + H_2O(l)$$

Salts with short carbon chains show mainly ionic character, and those with very long chains show mainly organic character.

3-) Halogenation reactions

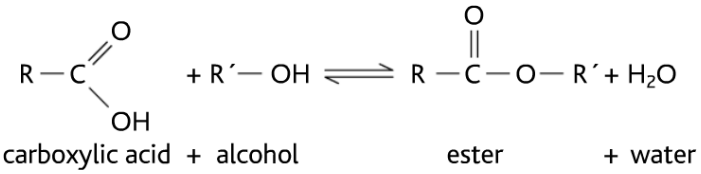
Carboxylic acids react with phosphorus(V) chloride to form acyl chlorides.



The reaction is accompanied by the white fumes of hydrogen chloride gas. This is commonly used as a test for –OH groups in an unknown compound.

4-) Esterification

Esters are one of several families of organic compounds that are direct derivatives of carboxylic acids. When a carboxylic acid is mixed with an alcohol in the presence of a strong acid catalyst, such as sulfuric acid, an ester is formed.



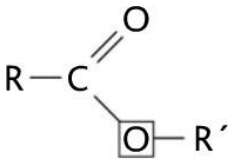
It can be considered as a condensation reaction – one between two molecules to form a larger molecule with the loss of a small molecule, in this case water. Esterification is relatively a slow reaction and is subject to equilibrium considerations. It can be more convenient to prepare the more reactive acyl chloride.

3 Carboxylic acid derivatives

1 ESTERS

Esters are volatile compounds. They do not form hydrogen bonds and so their melting and boiling temperatures are relatively low and they are not soluble in water or other polar solvents.

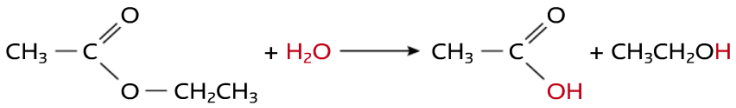
A distinct feature of an ester molecule is the oxygen atom which forms a bridge between the two parts. This oxygen bridge is formed as the carboxylic acid and alcohol molecules join. It was shown using radioactive O-18 atom that the **bridging oxygen in the ester comes from the alcohol molecule and not the carboxylic acid**.



2 REACTIONS OF ESTERS

1-) Acid hydrolysis

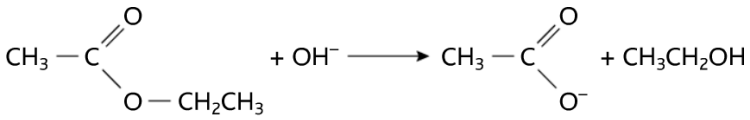
Esters can be split up by boiling with water and, much more effectively, by using a dilute acid. The dilute acid provides hydrogen ions, which catalyse the reaction.



ethyl ethanoate ethanoic acid ethanol

2-) Base hydrolysis

An ester can also be hydrolysed by boiling it with alkali solution, such as NaOH. This is a more efficient process because when the acid is released it is neutralised by alkali to form the sodium salt. This does not react with the alcohol.



ethyl ethanoate ethanoate ion ethanol

Soaps are produced by the action of sodium hydroxide on natural fats and oils that contain natural esters. This hydrolysis reaction is sometimes called saponification.

3-) Trans-esterification

In trans-esterification, the trans means transfer. It involves the interconversion of one carboxylic acid ester into one another. For example, a methyl ester becoming an ethyl ester.

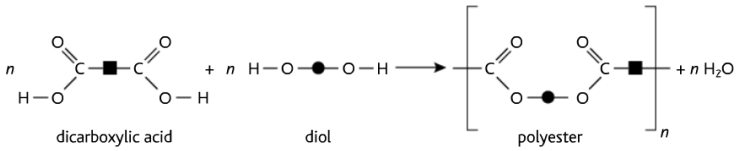
Uses of trans-esterification

- C=C double bond resists rotation, producing two types of isomers, cis and trans.

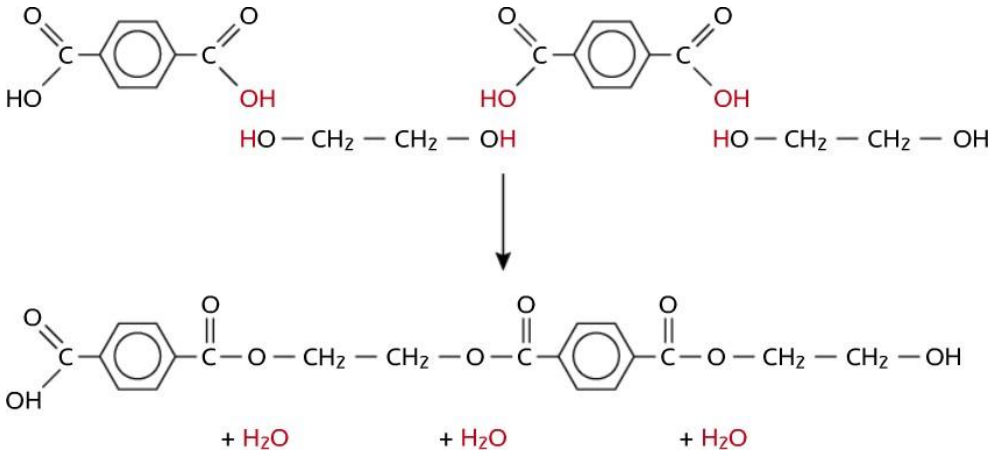
- Margarine is usually made by partial hydrogenation of liquid unsaturated oils and fats to make them more solid, but this increases the proportion of trans-fats.
- Only trans-fats increase the risk of coronary heart disease.
- Trans-esterification offers an alternative way of hardening unsaturated fats and oils, producing far fewer potentially harmful trans-fats.
- Biodiesel is made by reacting natural oils or fats, such as triglycerides in palm oil, with alcohols to form esters of the alcohol and glycerol. A base catalyst is used.
- Biodiesel is an alternative to fossil fuels and is renewable but requires agriculture land.

4-) Polyesters

If a carboxylic acid and a diol are used it is possible to form a condensation polymer.

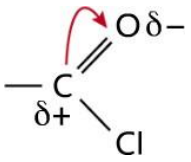


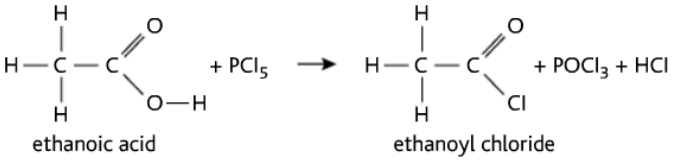
Polymerisation of ethane-1,2-diol and benzene-1,4-dicarboxylic acid



3 ACYL CHLORIDE AND THEIR REACTIONS

Acyl chloride are reactive compound produced when phosphorus(V) chloride reacts with a carboxylic acid. Acyl chlorides contain a carbonyl group with a chlorine atom attached to the carbon atom in the carbonyl group. The oxygen in the carbonyl group withdraws electrons from the double bond, giving the central carbon atom a {+ charge – making it susceptible to attack by nucleophiles.

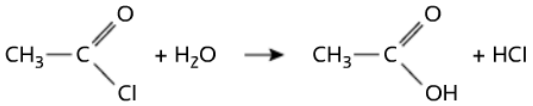




ethanoic acid — ethanoyl chloride

1-) Reaction with water

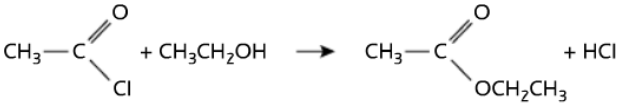
Acyl chlorides are hydrolysed rapidly with cold water. Hydrogen chloride reacts with water vapour in the air to give white fumes.



ethanoic acid

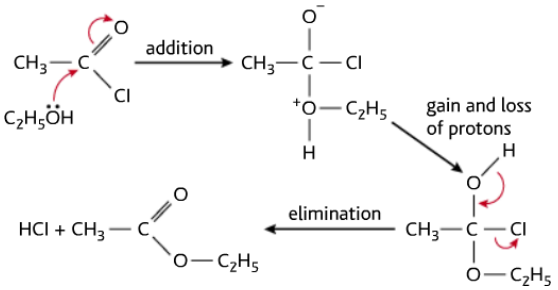
2-) Reaction with alcohols

Acyl chlorides react with alcohols to produce esters. These reactions take place on mixing the acyl chloride and the alcohol without heating.



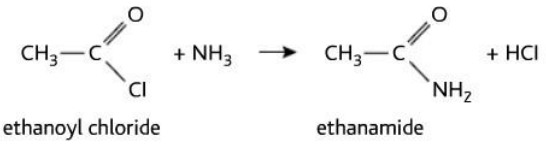
ethyl ethanoate

Mechanism for this nucleophilic addition/elimination reaction



3-) Reaction with concentrated ammonia

Acyl chlorides react with concentrated ammonia to produce amides. These reactions take place on mixing the reactants and without heating.



ethanoyl chloride ethanamide

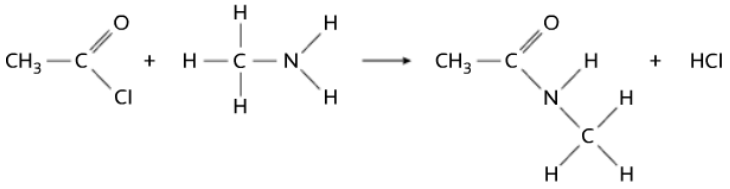
fig. 1.6.75 Reaction of acyl chlorides with ammonia.

Because of the acid/base nature of the products, a further reaction takes place:

$$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$$

4-) Reaction with amines

A similar reaction occurs between acyl chlorides and amines to produce a substituted amine.



methylamine *N*-methylethanamide

In naming compounds such as this, N-methyl means that a methyl group is attached to the nitrogen atom of the amide.

Spectroscopy and chromatography

1 Spectroscopy

Spectroscopy is used in chemical analysis – it is a non-invasive technique that can follow the extent of a reaction. In absorption spectroscopy, a sample absorbs electromagnetic radiation from a beam.

Infrared radiation

Infrared (IR) can be absorbed by molecules. **Each functional group absorbs at a different vibrational frequency, producing a characteristic peak in wavenumbers in the IR spectrum**.

Since IR spectra can show the presence or absence of functional groups, it is possible to judge the extent of a reaction in which the functional groups change by comparing the IR spectrum of the product with that of the starting materials. The product must have strong absorptions that are absent in the starting material, such as in the reaction of halogenoalkanes with potassium hydroxide to form alcohols. Alcohols have strong O–H and C–O absorptions which are absent in the halogenoalkanes.

Microwave absorption for heating

- Microwave heating is selective – it heats solvents or particular molecules within them, but avoids heating the container itself.
- Polar molecules rotate with the microwave field and collide, causing a heating effect while non-polar molecules are transparent to microwave radiation.
- Much higher reaction temperatures can be achieved, significantly speeding up rates of reaction, improving product yields and reducing energy requirements compared to conventional heating.

Radio waves in NMR

- NMR is Nuclear Magnetic Resonance.
- Protons can spin about their axes giving a residual magnetic spin that makes the nucleus of certain elements, such as hydrogen, align with a magnetic field.
- Hydrogen nuclei, ^{1}H, absorb energy at the frequency of the radio waves used in nmr spectroscopy.
- In a very strong magnetic field, the proton's spin can interact with the radio waves, causing resonance at a particular frequency.
- Nmr spectroscopy is used to determine the structure of molecules.
- Protons in different molecular environments – such as a single proton from ^{1}H nuclei in an OH group, or two protons from ^{1}H nuclei in a CH_2 group – give different peaks in the nmr spectrum.
- The relative areas under the peaks give information about the numbers of ^{1}H nuclei present in each molecular environment.

Chemical shifts

- Chemical shifts are the locations in an nmr spectrum where a nucleus absorbs energy (resonates).
- The shifts are measured relative to a reference sample, TMS which does not react with the rest of the sample but produced strong internal reference peak.
- The units of chemical shift are parts per million (ppm).

High-resolution nmr spectra

More information can be found by splitting or resolving the nmr peaks in a high-resolution nmr spectrum. These splitting patterns, called spin-spin coupling patterns, are due to the spin states of protons on an adjacent carbon atom.

A single nmr peak can be split into (n+1) parts by an adjacent group that has n protons, which are in chemically different molecular environments form the proton producing the original peak. This is called the **n+1** rule.

Ultraviolet

Ultraviolet (UV) and visible light are absorbed by molecules and ions giving a spectrum with characteristic absorption bands. Unknown materials can be identified by comparing their spectra with those of known materials.

When some materials absorb UV this causes homolytic fission, producing free radicals. Chlorine absorbs UV at a wavelength of 300 nm, but methane does not. Chlorine free radicals, which have an unpaired electron, can initiate free radical chain reactions.

Mass spectrometry

- Each peak corresponds to a particular species.
- The mass to charge ratio is given by m/z; z is usually taken as 1.
- The heights of the peaks correspond to the relative abundances of each species.
- The highest mass peak is likely to be the molecular ion; m/z corresponds to the relative molecular mass of the compound, M, when z=1.
- The fragmentation pattern for a compound can often help to identify the structure of the compound, or to distinguish between compounds such as isomers.

2 CHROMATOGRAPHY

Gas chromatography

Gas chromatography separates volatile components in a mixture so that they can be analysed and identified. It is used in industrial processes to monitor the presence or absence of materials at different stages of a process.

Samples are injected into the chromatography column and are carried along by the gas stream to the detector. The time taken to travel through the column is the retention time. Each component has its own characteristic retention time, which can be compared with known samples.

High performance liquid chromatography (HPLC)

HPLC improves the separation of components in a mixture, allowing more effective analysis. Flow times of a solvent through the HPLC column are speeded up using a pressure of 200-300 atm with strong stainless steel columns.

Separate components can be washed off the column using a solvent. UV spectra show if a component is dissolved in the solvent and each can be collected separately for analysis.

Redox and chemistry of the transition metals

1 Application of redox equilibria

1 TERMINOLOGY

Oxidation number: The oxidation numbers of the elements in a compound are the charges they would have if the electrons in each bond of the molecule or ion belonged to the more electronegative element. The oxidation number of an ion is the number of electrons that have been removed (cation) or added (anion). The oxidation number of an uncombined element or compound is zero.

- The oxidation number for an atom of any free (uncombined) element is ZERO.
- The oxidation number of an element in self-combination is always ZERO.
- In most hydrogen containing compounds, oxidation number of hydrogen is + 1.(Exception is when H combines with alkali metals or alkaline earth to form hydrides of metals such as: NaH, LiH, CaH_2. Then, the oxidation number of H is -1).
- In compounds involving the alkali metals, the elements are assigned oxidation number of +1.
- In compounds involving the alkaline earth metals, the elements are assigned oxidation number of +2.
- Oxygen is usually assigned an oxidation number of -2 for oxides. It has an oxidation number of -1 in peroxides (H_2O_2).
- Fluorine always has oxidation number of -1 in compounds. The other elements in that group are usually -1 in compounds with elements of low electronegativity.
- The sum of oxidation numbers of all the atoms in the formula for a neutral compound is ZERO.
- The sum of oxidation numbers of an ion or complex ion is the same as the charge on that ion.
- Negative oxidation number in compounds of two unlike atoms are assigned to the more electronegative atom.

Redox reactions: A redox reaction is one involving both reduction and oxidation. A process involving a loss of electrons is an oxidation reaction, and a process involving the gain of electrons is a reduction reaction.

Half-reaction: Half-equations are ionic equations used to describe either the gain or the loss of electrons during a redox process. Half-equations help to show what is happening during a redox reaction.

Oxidising agents: They take electrons and are reduced when they react.

Reducing agents: They give up electrons and are oxidised when they react.

2 REDOX TITRATIONS

In a redox titration, an oxidising agent reacts with a reducing agent. During the titration, the aim is to measure the volume of a **standard solution** of an oxidising agent or a reducing agent that reacts exactly with a measured volume of the other reagent.

Redox titration 1: Potassium manganate(VII) and iron

$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$

- Potassium manganate(VII) is a powerful oxidising agent and has intense **purple colour** in aqueous solution.
- In acid solution, it is reduced to almost **colourless** manganese(II) salts.
- A standard solution of potassium manganate(VII) is titrated against the solution of iron(II) ions of unknown concentration.
- This titration is self-indicating, so no additional indicator is needed.
- The end-point is when all the iron(II) has been oxidised to iron(III). The first excess of manganate(VII) gives a permanent pink colour – this is the end-point.
- The reaction stoichiometry gives a mole ratio of 5 mol Fe^{2+} to 1 mol MnO_4^-.

Redox titration 2: Sodium thiosulfate and iodine

$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

- Iodine in solution of potassium iodide is a dark **brown colour**.
- Addition of sodium thiosulfate results in a light brown/yellow colour as the iodine is reduced giving a **colourless** solution at the end-point.
- Near the end-point, while the solution is still pale yellow, starch indicator is added giving a **blue-black** solution. The end-point change is now blue to colourless, showing that all the iodine has reacted.
- This titration can be used to find the concentration of an oxidising agent that oxidises iodine ions to form iodine – copper(II) ions for example.

To estimate the percentage of copper in an alloy, the copper alloy is dissolved, and the resulting solution is reacted with **excess potassium iodide solution** to produce **iodine**. The liberated iodine is titrated with standard sodium thiosulfate.

- A weighed sample of the alloy is reacted with nitric acid giving a solution containing Cu^{2+}.
- This is reacted with an excess of potassium iodide solution:

$2Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI(s) + I_2(aq)$

- The amount of liberated iodine is estimated by titrating with standard sodium thiosulfate.

- Overall the reaction stoichiometry shows that 2 moles of Cu^{2+} gives 1 mole of I_2, which is reduced by 2 moles of $S_2O_3^{2-}$; this gives a 1:1 mole ratio.

Measurement of uncertainty and implications

Uncertainty can be caused by poor technique or by the limits of precision of the apparatus.

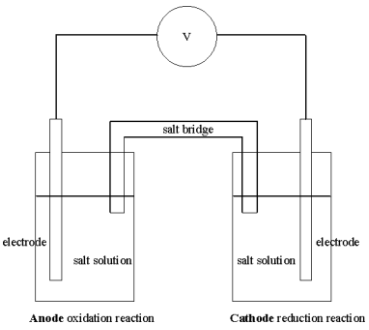
- Remember to quote a mean titre or the calculated solution concentration to the same number of significant figures as the least precise measurement in the experiment.
- Repeating the experiment will improve the reliability of the data, but not the accuracy if the same conditions and apparatus are used.
- The larger the measurement, the smaller the percentage error – when using apparatus of comparable quality.
- Be careful about any assumptions made – e.g. about the alloy sample:
  - Alloy composition is uniform throughout the sample.
  - Sample chosen is representative e.g not a corroded surface.

  They can introduce systematic errors and inaccuracy in the calculated value.

3 REDOX AND ELECTROCHEMICAL CELLS

The competition for electrons in redox reactions is not always clear cut. Chemists developed the idea of electrode potentials, which can be used to determine if a redox reaction will take place between two systems, and which direction it will go in.

Electrochemical cells



Electrochemical cells produce an electric potential difference from a redox reaction. In an electrochemical cell, the two half reactions happen in separate half cells. The electrons flow from one cell to the other through a wire connecting the electrodes. The electric circuit is completed by a salt bridge connecting the two solutions. The salt bridge makes an electrical connection between the two halves of the cell by allowing ions to flow while preventing the two solutions from mixing. At its simplest, a salt bridge consists of a strip of filter paper soaked in saturated potassium nitrate solution and folded over each of the two beakers.

Chemists measure the tendency for the current to flow in the external circuit by using a high-resistance voltmeter to measure the maximum cell e.m.f. when no current is flowing. The electromotive force (e.m.f.) of a cell measures the maximum voltage produced by an electrochemical cell. The symbol for e.m.f. is E and its SI unit is the volt(V). The e.m.f. is the energy transferred in joules per coulomb of charge flowing through the circuit connected to a cell.

4 ELECTRODE POTENTIALS

When we measure the e.m.f. of a cell, we imagine that it arises from the competition for electrons between the two half-cells. Each half-cell reaction will have its own tendency to attract electrons, a tendency that is measured by the electrode potential of the half-cell.

- The electrode potential is the maximum e.m.f. across the half-cell, in volts.
- The standard electrode potential, E_{cell}, is the e.m.f. between the two half-cells used measured under standard conditions.

Electrode potentials are relative to each other. A standard half-cell (or reference electrode) is needed to establish the individual cell potentials for the half-cells. The standard hydrogen half-cell has a defined e.m.f. of zero volts under standard conditions. This consists of **hydrogen gas at 1 atm pressure and 298 K bubbling around a platinum electrode in 1.00 mol dm^{-3} H$^+$(aq) ions**. So, other cells can be compared with it to give standard electrode potentials. E_{cell} is the difference between the standard electrode potentials of the two half-cells.

$$2H^+(aq, 1.00\,mol\,dm^{-3}) + 2e^- \rightleftharpoons H_2(298\,K, 1\,atm)$$
$$E^\ominus = 0.00V$$

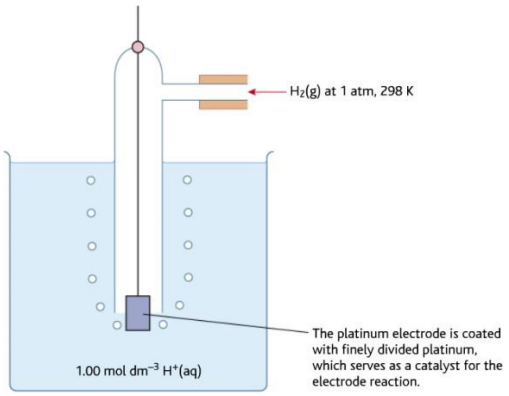

H2(g) at 1 atm, 298 K
The platinum electrode is coated with finely divided platinum, which serves as a catalyst for the electrode reaction.
1.00 mol dm⁻³ H⁺(aq)

fig. 2.1.14 The standard hydrogen half-cell.

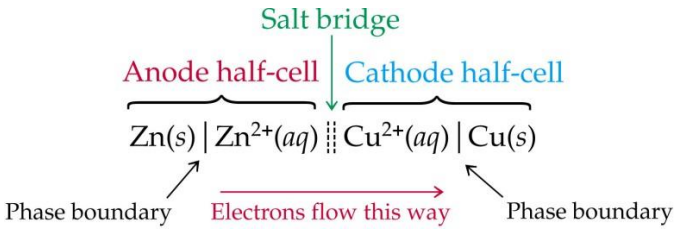
Conditions and conventions in electrochemisty

The conditions chosen to measure standard electrode potentials are the same as those for other standard measurements.

- All solutions have unit activity (effectively 1.00 mol dm^{-3} for our purposes)
- All measurements are made at 1 atmosphere pressure
- All measurements are made at 298 K

Drawing full diagrams of electrochemical cells is not necessary – there is a shorthand convention.

- The metal electrodes are written at the ends, with a line separating them from their aqueous ions.
- The salt bridge is shown in the centre as a vertical dotted line.



Calculating electrode potentials

Make the more negative potential the left-hand half-cell (LHS), to give the rule:

$$E^\circ_{cell} = E^\circ_{RHS} - E^\circ_{LHS}$$

5 Oxidising and Reducing Agents

The standard electrode potential of half-cell is a measure of the oxidising power or reducing power of the species in it – in other words, the ability to compete for electrons. In general the stronger an oxidising agent, the more positive its electrode potential. A strong reducing agent has a large negative electrode potential.

6 Feasibility and Extent of Reactions

When comparing two redox systems, a reaction will take place if:

- The stronger reducing agent with the more negative E° is on the right-hand side of the equation.
- The stronger oxidising agent with the more positive E° is on the left-hand side of the equation.

For a reaction to be feasible, the E°_{cell} value must be positive, and once the value reaches about +0.6V, the reaction is extremely likely to progress.

E°_{cell} is directly proportional to the total entropy change and ln k in a reaction. Therefore, the more positive the value of E°_{cell}, the more energetically favourable is the reaction.

To make a prediction about a reaction, you need to write down the two half-equations for it.

- Write down the equation for the reaction.
- Split the equation into two half-equations and write down the electrode potentials.
- Add the half-reactions and the electrode potentials together.

- The sign of the cell e.m.f. value indicates whether the reaction will occur spontaneously or not.

An E°_{cell} value can tell you more than if the reaction is likely to happen or not happen – it also gives you an idea of the extent of the reaction. As a general principle:

- if $E^{\ominus}_{cell} > +0.6V$ then the reaction should go to completion
- if $0 < E^{\ominus}_{cell} < +0.6V$ then the products predominate
- if $-0.6V < E^{\ominus}_{cell} < 0$ then the reactants predominate
- if $E^{\ominus}_{cell} < -0.6V$ then there is no reaction.

E°_{cell} is related to the probability that a reaction will take place. It is not affected by the quantity of materials in the reacting mixture.

7 LIMITATIONS OF STANDARD ELECTRODE POTENTIALS

Just like enthalpy changes, standard electrode potentials must be used with care when predicting the likelihood of a reaction. Both ΔH and E° are concerned with the energetic stability of a substance, not its kinetic stability – so they can tell you whether a reaction is possible, but not whether it happens fast enough to be noticeable.

Another important point about standard electrode potentials is that conditions under which the reaction occurs may be different from standard conditions. Temperature and concentrations are two factors that may be particularly important in influencing a reaction.

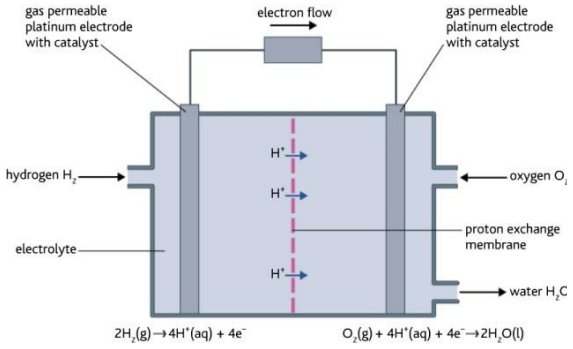
Therefore:

- A reaction with a positive $E^{\ominus}_{cell}$ value may not actually take place. Predictions can be made as to the feasibility of these equilibrium reactions but they give no indication of the rate, which may be very slow – because of a high activation energy, for example.
- The conditions used may be different from standard conditions and so the actual electrode potentials will differ from the standard electrode potentials.
- Standard electrode potentials apply to aqueous equilibria. There are many reactions that take place that are not in aqueous solutions.

	Reaction does not take place	Reaction to the left	Equal amounts of reactants and products	Reaction to the right	Reaction to completion
K_c	$< 10^{-10}$	0.01	1	100	$>10^{10}$
$E^{\ominus}$	< –0.6	approx. –0.1	0	approx. +0.1	> +0.6
ΔS_{total}	< –200	approx. –40	0	approx. +40	> +200

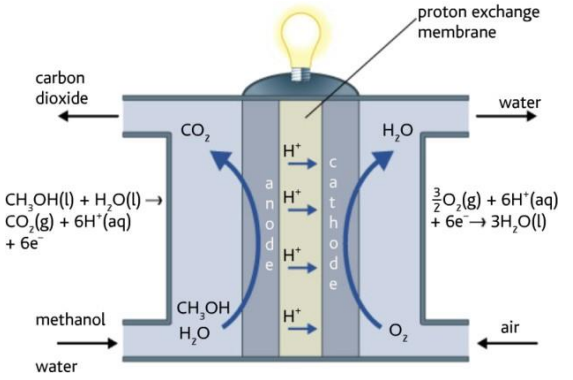
8 FUEL CELLS

Hydrogen fuel cells



Two electrodes are separated by a membrane, which allows hydrogen ions to pass through but not hydrogen and oxygen molecules. The electrons released by the reaction at the hydrogen electrode are used up at the oxygen electrode. The potential difference set up pushes electrons through the external circuit, where they do work.

Methanol-based fuel cells



Methanol is a highly-flammable, poisonous liquid alcohol. The fuel cell operates at a temperature between 90°C and 120°C and uses the oxidation of methanol on a catalyst layer to form carbon dioxide. The proton exchange membrane is often made from Nafion. Electrons are transported through an external circuit from anode to cathode, providing power to connected devices.

Sources of fuels for use in fuel cells

- Hydrogen can be obtained from water or brine by electrolysis.
- Natural gas (methane) can also be a source of hydrogen.
- Alcohols can be obtained by fermentation of sugars or by the hydration of alkenes obtained from crude oil.

Advantages and limitations of fuel cells

- Fuel-cell vehicles are very efficient – more efficient than petrol engines.
- Fuel cells produce no carbon dioxide emissions or pollutants such as CO at the point of use – although fuel production and pressurisation of hydrogen does cause pollution.
- During the manufacture of hydrogen from methane, the carbon in the methane is converted to carbon dioxide.
- Fuel cells currently have a limited lifetime and are expensive to replace.
- Hydrogen fuel is gaseous and, hence, difficult to transport and store – by liquefaction at ultra-low temperatures on in high-pressure storage systems or by solid state adsorption.

9 BREATHALYSER TECHNOLOGY

In old-fashioned breathalysers, ethanol in a driver's breath was detected by a colour change in the reduction of orange dichromate(VI) ions to green chromium(III) ions:

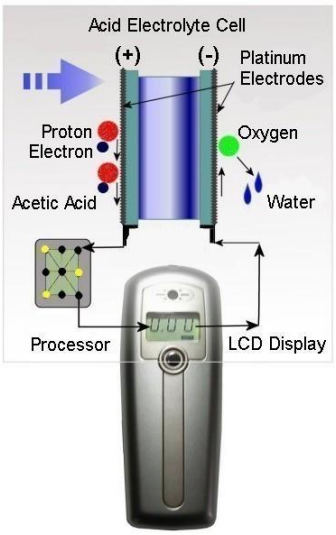
$$3C_2H_5OH(g) + 2Cr_2O_7^{2-}(aq) + 16H^+(aq) \rightarrow 3CH_3COOH(aq) + 4Cr^{3+}(aq) + 11H_2O(l)$$

The sensitivity of this simple breathalyser was limited and so was open to question when a driver was taken to court. The amount of ethanol in the breath depends on the concentration in the blood, but mouth alcohol can give error in readings.

Drivers can also be asked to provide a breath sample for infrared (IR) analysis at a police station. Ethanol has an easily recognizable IR spectrum with a peak at 2950 cm^{-1} that corresponds to the C – H absorption frequency. The OH group in ethanol is not used for IR analysis because the presence of water in breath affects the reading.

Fuel-cell breathalyser

- This device detects a chemical reaction of ethanol inside a fuel cell.



- Exhaled air flows past one side of the cell – the platinum electrode oxidises any ethanol to ethanoic acid, releasing both protons and electrons.
- A meter measures the current flow.
- The protons combine with oxygen on the other side of the fuel cell, forming water.
- The more alcohol in the exhaled breath, the more is oxidised and the greater the measured current.

Fuel-cell breathalysers are not as reliable as systems using IR or mass spectroscopy, or the measurement of blood alcohol content from blood samples.

2 Transition metals and their chemistry

1 INTRODUCTION TO TRANSITION METALS

Transition metals are commonly used in everyday life. A rather vague definition of transition metals is elements found between the s block and the p block. However, this causes problems when the structure, properties and reactions of the elements are considered, because not all of the metals fit in. To overcome this, a more effective definition is:

Transition metals: Elements which form one or more stable ions which have incompletely filled d orbitals.

Based on this definition transition metals have a few properties in common:

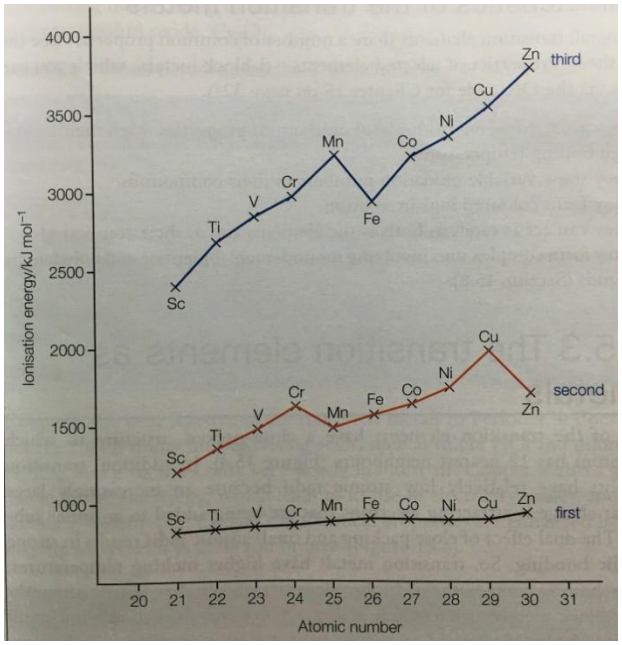
- They are all hard metals with high melting and boiling temperatures.
- They show variable oxidation number in their compounds.
- They tend to form coloured compounds and ions in solution.
- Many show catalytic activity.
- They form complex ions involving monodentate and bidentate ligands.

Scandium and zinc metals do not show transitional properties. Although these two elements are hard metals, they do not show multiple oxidation numbers, they form white rather than coloured compounds and they do not act as catalysts. The differences in their properties exist because:

- A scandium atom loses three electrons, forming a Sc^{3+} ion (with the same electronic configuration as argon [Ar]).
- A zinc atom loses the outer $4s^2$ electrons, giving a Zn^{2+} ion (with the electronic configuration [Ar] $3d^{10}$).

Neither element forms an ion with an incomplete d sub-shell and so they are not considered to be true transition elements – reflecting the fact that their chemical behaviour differs from that of the other elements in the d block.

2 ELECTRON CONFIGURATION OF TRANSITION METALS



An ionisation energy is the energy needed to remove one mole of electrons from one mole gaseous atoms, or ions, of an element.

General trend: From Sc to Zn, the nuclear charge is increasing while electrons are being added to an inner shell. The increasing nuclear charge attracts the outer shell electrons more strongly and so the ionisation energies increase from Sc to Zn. However, the electrons added to the inner 3d sub-shell increase the shielding of outer electrons and this restricts the increase in ionisation energies.

Zinc

- The first ionisation of zinc is more endothermic than that of the other d-block elements in Period 4.
- The electronic configuration of zinc atoms is more stable than those of other elements.
- The electronic configuration zinc atoms is [Ar] $3d^{10}4s^2$. It has a completely full third shell and a filled 4s sub-shell. None of the other elements have such a stable structure.

Copper

- The electronic structure of Cu^+ ions must be more stable than those of the equivalent ions of its neighbours.
- The electronic configuration of Cu is [Ar] $3d^{10}4s^1$ and that of Cu^+ is [Ar] $3d^{10}$. This latter structure with a completely full third shell is relatively stable.

Chromium

- The electronic structure of Cr^+ ions must be more stable than those of the equivalent ions of its neighbours.
- The electronic configuration of Cr is [Ar] $3d^5$ $4s^1$ and that of Cr^+ is [Ar] $3d^5$. This latter structure with a half-filled 3d sub-shell and an even distribution of charge in the five 3d orbitals is more stable than the equivalent ions of its neighbours (V – [Ar] $3d^3 4s^1$ and Mn^+ - [Ar] $3d^5 4s^1$).

Note: Metal ions with half-filled or fully-filled d orbitals have relatively high ionisation energies.

3 CHARACTERISTICS OF TRANSITION METALS

The most common oxidation number of most of the elements is +2, due to the loss of the outer two 4s electrons. However, the underlying d orbitals are very close to the 4s level, and so it is relatively easy to lose electrons from these as well.

This means that several different ions of the same element are possible because the atoms can lose different numbers of electrons. The first period of the transition elements always lose their 4s electrons first on forming compounds, and variable numbers of the 3d electrons may be lost as well. The interconversions between one oxidation number and another are an important aspect of transition metal chemistry. This is frequently reflected by colour changes in solutions of the complex ions.

Element	Most common oxidation numbers	Electronic configuration of most common ions			Examples of compounds
Ti	+2, +3, +4	[Ar] $3d^1$	[Ar]		Ti_2O_3, $TiCl_4$
V	+1, +2, +3, +4, +5	[Ar] $3d^2$	[Ar]		VCl_3, V_2O_5
Cr	+1, +2, +3, +4, +5, +6	[Ar] $3d^5$	[Ar]		$CrCl_3$, CrO_3
Mn	+1, +2, +3, +4, +5, +6, +7	[Ar] $3d^5$	[Ar] $3d^3$	[Ar]	$MnCl_2$, $KMnO_4$
Fe	+1, +2, +3, +4, +6	[Ar] $3d^6$	[Ar] $3d^5$		FeO, $FeCl_3$
Co	+1, +2, +3, +4, +5	[Ar] $3d^7$	[Ar] $3d^6$		CoO, $CoCl_3$
Ni	+1, +2, +3, +4	[Ar] $3d^8$			$NiCl_2$
Cu	+1, +2	[Ar] $3d^{10}$	[Ar] $3d^9$		Cu_2O, $CuSO_4$

Transition metals usually show their highest oxidation numbers when they are combined with oxygen or fluorine, the most electronegative element. The highest oxidation numbers of all the elements up to and including manganese correspond to the involvement in bonding of all of the electrons outside the argon core. Beyond manganese the 3d electrons are held more strongly because of the increasing nuclear charge and so, by and large, the common oxidation numbers involve the 4s sub-shell only.

When the elements exhibit very high oxidation numbers, they do not form simple ions. Either they are involved in covalent bonding or they form polyatomic ions.

Forming of coloured ions in solution

Most of the transition metals form compounds which dissolve in water to form coloured solutions. Changes in the colour of solutions can alert us to a change in oxidation number of the ion. Where the ion has a $3d^0$ or $3d^{10}$ arrangement, the solution of the ion is colourless.

Ion	Name of ion	Oxidation number	Colour of solution
V^{2+}	Vanadium(II)	+2	Purple
V^{3+}	Vanadium(III)	+3	Green
VO^{2+}	Oxovanadium(IV)	+4	Blue
VO_2^+	Dioxovanadium(V)	+5	Yellow

table 2.2.4 The oxidation numbers of vanadium.

The colour of the solution is due to electrons absorbing photons of certain frequencies from visible light. The energy of each of these photons matches the energy needed for one electron to jump from a lower to a higher energy orbital. The frequencies of visible light remaining after this absorption give the solution its colour.

Forming transition metal complexes

When metals form compounds in the usual way it involves formation of ionic bonds. Complex formation involves the atoms forming dative covalent (also known as co-ordinate) bonds. These are bonds in which both bonding electrons come from the same atom.

As a result of their small size, the d-block ions have a strong electric field around them. This field attracts other species that are rich in electrons. Complex ions are formed when the central metal ion is surrounded either by anions or by molecules that act as electron-pair donors. These electron-pair donors are called ligands.

Ligands must be either anions or neutral molecules. Most importantly, **they must have a lone pair of electrons available for donation**. Common anions that act as ligands include:

- Halide ions (F^-, Cl^-, Br^-, I^-)
- Sulfide ion (S^{2-})
- Nitrate(V) ion (NO_3^-)
- Nitrate(III) ion (NO_2^-)
- Cyanide ion (CN^-)
- Hydroxide ion (OH^-)
- Thiocyanate ion (SCN^-)
- Thiosulfate ion ($S_2O_3^{2-}$)
- Ethanoate ion (CH_3COO^-)

Neutral molecules that act as ligands include:

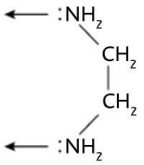
- H_2O
- NH_3
- CO

The number of ligands involved in a complex ion varies from element to element. When the formula of a complex ion is given, the metal ion always comes first followed by the ligands. **The charge on the complex ion is the sum of the charge on the metal ion and the charges on the ligands.** This means that when the ligands are neutral molecules, the charge on the complex ion is the same as the charge on the metal ion, but when the ligands are anions then the charge will be different.

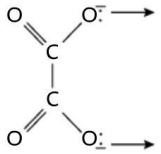
The number of lone pairs attached to the metal ion is called the coordination number and it determines the number of ligands which may be attached to the metal ion.

Polydentate ligands

All the ligands mentioned so far have been monodentate ligands, which means that they join to the metal ion by one atom only. Other ligands are bidentate – they join to the metal ion by two atoms;

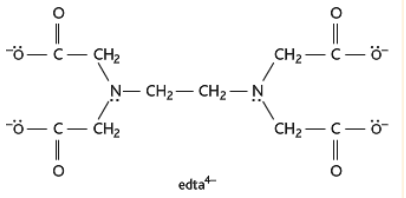


1, 2-diaminoethane



ethanedioate ion

Other ligands are polydentate, which means they may attach to the transition metal by more than two atoms, leading to the formation of complex ring structures – for example ethylenediaminetetraacetic acid (EDTA).



edta^{4-}

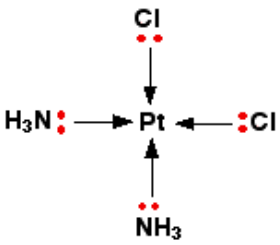
4 THE GEOMETRY OF COMPLEX IONS

The complex ions of the transition metals can form a number of different geometrical shapes including linear, planar, tetrahedral and octahedral. Metal ions with a coordination number of 2, such as silver and copper, generally form complexes with a linear structure.

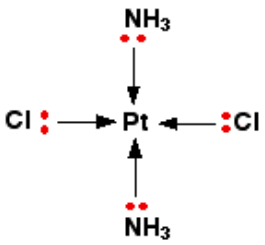
Metal ions with a coordination number of 4 produce complex ions with one of the two possible geometries – it depends on whether the d orbitals are complete or not. So, a transition metal with a coordination number of 4 and complete d orbitals shows tetrahedral geometry. A coordination number of 4 combined with incomplete d orbitals, as in copper, nickel and platinum complexes, sometimes results in square planar geometry.

The most common coordination number for the transition elements is 6, and these complexes are almost all octahedral.

Comples	Coordination number	Bond angle	Shape
$[CuCl_2]^-$	2	180°	Linear
$[Pt(NH_3)_2Cl_2]$	4	90°	Planar
$[CrCl_4]^-$	4	109.5°	Tetrahedral
$[Cr(NH_3)_6]^{3+}$, $[Cu(H_2O)_6]^{2+}$	6	90°	Octahedral



the "**cis**" form



the "**trans**" form

Naming complex ions

- Identify the number of ligands around the central cation using the prefixes: mono-, di-, tri-, tetra-, and so on.
- Name the ligand using names ending in –o for anions, e.g chloro for Cl^-, fluoro- for F^-, cyano for CN^-, hydroxo- for OH^-. Use aqua for H_2O and ammine for NH_3.
- Name the central metal ion using the normal name of the metal for positive and neutral complex ions and Latinised name ending in –ate for negative complex ions, e.g. ferrate for iron, cuprate for copper, argentite for silver.
- Finally, add the oxidation number of the central metal ion.

5 CHEMISTRY OF COPPER

Copper is a transition metal with electronic configuration [Ar] $3d^{10}4s^1$. It forms compounds with oxidation numbers +1 and +2.

- Copper(I) [Ar] $3d^{10}$
- Copper(II) [Ar] $3d^9$

In the +1 oxidation number, where a full set of filled 3d orbitals is present, compounds are often white in colour and do not have the typical properties of transition metal compounds. But in the +2 oxidation number it shows typical transition metal properties. The higher charge on the copper ion gives stronger bonding, compensating for the extra energy required to remove an electron from the 3d orbital in addition to one from the 4s orbital.

Copper(I) and disproportionation

Copper(I) is unstable in aqueous solution and exists only:

- At high temperatures
- When insoluble and precipitated
- In complexes

In aqueous solution, copper(I) compounds disproportionate. Disproportionation is the oxidation and reduction of the same element in the same reaction. For example, Cu^+ (aq) disproportionates in solution:

$$Cu_2SO_4(aq) \rightarrow Cu(s) + CuSO_4(aq)$$

The electrode potentials explain why:

$$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq) \qquad E^\ominus = +0.15V$$

$$Cu^+(aq) + e^- \rightleftharpoons Cu(s) \qquad E^\ominus = +0.52V$$

$$2Cu^+(aq) \rightarrow Cu(s) + Cu^{2+}(aq) \qquad E^\ominus_{cell} = +0.67V$$

Copper(I) ions can be stabilised in solution by adding concentrated hydrochloric acid to form a complex:

$$CuCl(s) + Cl^-(aq) \rightarrow [CuCl_2]^-(aq)$$
dichlorocuprate(I)

Copper(I) chloride is prepared by boiling copper(II) chloride with concentrated hydrochloric acid. Initially, the tetrachlorocuprate(II) complex ion is formed:

$$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightarrow [CuCl_4]^{2-}(aq) + 6H_2O(l)$$

This is then reduced to the dichlorocuprate(I) ion by boiling with copper:

$$[CuCl_4]^{2-}(aq) + Cu(s) \rightarrow 2[CuCl_2]^-(aq)$$

When this mixture is poured into cold water a white precipitate of copper(I) chloride is formed:

$$[CuCl_2]^-(aq) \rightarrow CuCl(s) + Cl^-(aq)$$

Copper(I) iodide is precipitated as a white solid (tinged by the iodine also formed) when potassium iodide solution is added to copper(II) sulfate solution:

$$2CuSO_4(aq) + 4KI(aq) \rightarrow 2CuI(s) + 2K_2SO_4(aq) + I_2(aq)$$

or $2Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI(s) + I_2(aq)$

Copper(II) and ligand exchange reaction

Copper(II) is the more stable state of the element in copper compounds. In an aqueous solution of copper(II) sulfate, copper(II) ions are surrounded by six water molecules to form the octahedral complex hexaaquacopper(II).

When ammonia solution is added, a precipitate of hydrated copper(II) hydroxide is formed:

$$[Cu(H_2O)_6]^{2+}(aq) + 2NH_3(aq) \rightarrow [Cu(H_2O)_4(OH)_2](s) + 2NH_4^+(aq)$$

Adding more ammonia solution causes ligand exchange with four water molecules in the complex being replaced by ammonia molecules. This produces a deep inky-blue complex of tetraaminecopper(II) ions:

$$[Cu(H_2O)_4(OH)_2](s) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 2OH^-(aq) + 2H_2O(l)$$

6 CHEMISTRY OF CHROMIUM

Chromium is a silvery, lustrous transition metal that is hard, brittle and very resistant to corrosion. Its atoms have the electron configuration [Ar] $3d^5$ $4s^1$. Chromium is very unreactive and it provides an excellent protective covering for other metals.

Chromium has various oxidation numbers in its compounds, the most common being +2, +3 and +6:

- Chromium(II) [Ar] $3d^4$
- Chromium(III) [Ar] $3d^3$
- Chromium(VI) [Ar]

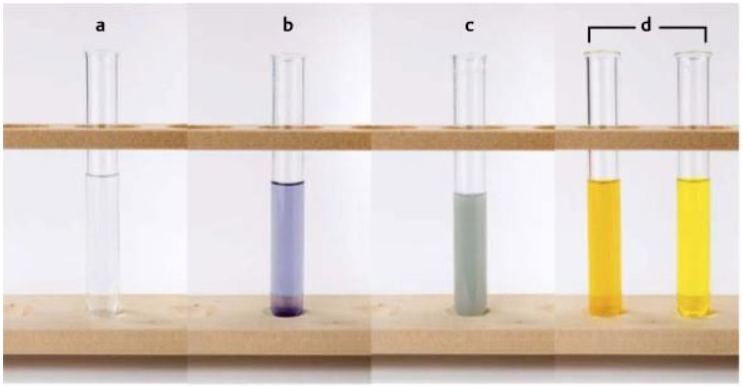


fig. 2.2.17 Chromium compounds produce many brightly coloured solutions.

a When chromium metal is dissolved in a dilute, oxygen-free, non-oxidising acid the pale blue colour of the Cr^{2+} ion is seen.

b The violet colour of this solution of chrome alum [$K_2SO_4 \cdot Cr(SO_4)_3 \cdot 2H_2O$] is typical of the $Cr(H_2O)_6^{3+}$ ion.

c The addition of an alkali to a solution in (b) gives a green solution containing $Cr(H_2O)_2(OH)_4^-$ ions.

d The dichromate ion ($Cr_2O_7^{2-}$), which predominates in acidic solution, has a reddish-orange colour; the chromate ion (CrO_4^{2-}) formed in alkaline solutions has a bright yellow colour.

Facts

- Cr^{2+} has a pale blue colour in aqueous solution. It is very easily oxidised to the most stable oxidation number of chromium +3.
- The Cr^{3+} ion forms a complex with water $[Cr(H_2O)_6]^{3+}$, and the violet/blue-grey colour of this complex is typical of solutions of many chromium(III) compounds.
- The hydrated Cr^{3+} ion often gives a green solution when it is involved in reactions. This is because ligand exchange reactions often take place, with one of the water molecules being replaced by a negative ion from the solution, often a sulfate or chloride ion.
- Chromium(III) ions also tend to exhibit amphoteric characteristics.
- Two of the most common ions in which chromium has oxidation number +6 are the chromate(VI) ion, which is bright yellow, and the dichromate(VI) ion, which is orange.

$$CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

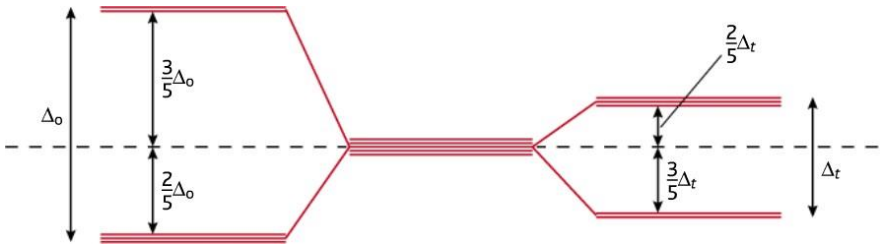
7 CRYSTAL FIELD THEORY

When white light is shone onto a substance, light of a particular frequency may be absorbed. Colour at this frequency is removed from white light – for example, when red light is absorbed, the solution will appear blue.

In an isolated transition metal ion there are five d orbitals, all of equal energy. The addition of ligands to the ion **splits the five orbitals into two groups of different energies**.

Whenever transition metal ions are surrounded by ligands, the electron transitions between the split energy levels in partly filled d sub-shells give these ions the characteristic colours of hydrated complex ions and hydroxides. Similar electron transitions are not possible for either d^0 or d^{10} ions, such as Sc^{3+} or Zn^{2+}, which therefore form colourless compounds and aqueous solutions.

Changing the ligand changes the amount of splitting (the size of the energy gap) and so changes the colour of the complex ion.



8 LIGAND EXCHANGE AND STABILITY OF COMPLEX IONS

When a ligand is exchanged for a water ligand, we can write a stability constant, known as K_{stab}.

$$K_{stab} = \frac{[[Cu(H_2O)_2(NH_3)_4]^{2+}(aq)]}{[[Cu(H_2O)_6]^{2+}(aq)] \times [NH_3(aq)]^4}$$

If K_{stab} has a higher value then the new complex is more stable than the one it replaced. When a single EDTA ligand replaces six separate ligands, the EDTA complex will have a high value of K_{stab}.

The additional stability of complex ions following ligand exchange results from an increase in entropy. When monodentate ligands are replaced by polydentate ligands, the total number of species increases – this results in a positive entropy change.

9 USES OF TRANSITION METALS

Transition metals and their compounds are often good catalysts. In many industrial processes, the reactants are adsorbed temporarily on to the catalyst surface. When the reaction is complete, the products diffuse away leaving the catalyst surface available again. This is an example of heterogeneous catalysis. Heterogeneous catalysts can be poisoned when other materials bind permanently to their surfaces, preventing any other reaction.

The variable oxidation state of transition metal ions allows them to bind to reactants to give reaction intermediates. Although the metal ions take part in the mechanism, they are unchanged at the end of the reaction, thus are classified as catalysts.

Catalytic converters

Catalytic converters use a fine coating of platinum catalyst supported on a heat-resisting ceramic honeycomb material to give a large surface area.

Advantages	Disadvantages
Reduce air pollution and smog by unburnt or incompletely combusted fuel, removing nitrogen oxides and carbon monoxide	• Reduce fuel economy by several per cent • Catalyst can be poisoned by just one tank of leaded petrol • May take time to warm up to working temperature, releasing pollutants

Chemical research on catalysts

New and improved catalysts can have many benefits:

- Lower energy use in industrial processes
- Improved atom economy
- Use of waste materials from other processes
- Reduced environmental pollution

This is why research scientists are actively seeking and improving potential catalysts for the future.

For example, ethanoic acid can be prepared from butane and naphtha from crude oil using cobalt(II) ethanoate catalyst. However, there are many by-products including ethanoic acid, methanoic acid, propanoic acid and propanone. An alternative process producing ethanoic acid from methanol and carbon monoxide has a much higher atom economy because there are no by-products.

It is important that published research findings are as reliable as possible:

- New research must have peer-group review – other specialists assess the data before it is accepted for publication.

- New results must be able to be repeated by other scientists to check the new conclusions.

Most scientific research is collaborative – groups of scientists work together sharing ideas and learning from published theories and data.

Transition metal compounds have made possible some valuable new products:

- A platinum compound, cis-platin, which is a powerful anticancer drug
- Polychromic sunglasses have a thin reflective coating, often of chromium – the sunglasses can adjust to light conditions, becoming darker in bright sunlight and reducing glare.
- Photochromic lenses respond specifically to UV in sunlight – molecules in the lenses – associated with silver halides, change shape according to the UV intensity. In artificial light, the lenses remain transparent.

10 OBSERVATIONS ON TRANSITION METAL IONS

Aqua ion	Ion colour	NaOH(aq)	Excess NaOH(aq)	NH_3(aq)	Excess NH_3(aq)
Cr^{3+}	Green	Green ppt	Soluble green	Green ppt	Green ppt
Mn^{2+}	Pink	Cream to brown ppt	Insoluble	Cream to brown ppt	Insoluble
Fe^{2+}	Pale green	Dark green ppt	Insoluble	Dark green ppt	Insoluble
Fe^{3+}	Yellow or brown	Rusty red ppt	Insoluble	Rusty red ppt	Insoluble
Ni^{2+}	Green	Green ppt	Insoluble	Green ppt	Blue solution
Cu^{2+}	Blue or green	Blue ppt	Insoluble	Blue ppt	Deep blue solution
Zn^{2+}	Colourless	White ppt	Soluble	White ppt	Soluble

Transition metal ions form complexes, often coloured, which allow them to be identified in qualitative observation tests. Addition of either aqueous sodium hydroxide or ammonia solution to transition metal aqua ions forms metal hydroxide precipitates, which are coloured.

$$[Co(H_2O)_6]^{2+} + 2OH^-(aq) \rightarrow [Co(H_2O)_4(OH)_2](s) + 2H_2O(l)$$

A few metals, such as zinc and chromium, form a precipitate that dissolves by further reaction with excess sodium hydroxide, giving a solution again. This is called amphoteric behaviour – the metal hydroxides can react with both acids and bases.

An excess of ammonia solution can cause ligand exchange with many transition metal complexes, giving a new ammine complex. The change in ligand causes a colour change due to different splitting of d-orbital energies. (Ammines are complexes of ammonia.)

Organic chemistry – arenes, nitrogen compounds and synthesis

1 Arenes: benzene

1 THE STRUCTURE OF THE BENZENE RING

The use of bond energies and the concept of enthalpy changes (both theoretical and real) during the course of reactions help us predict the outcome of particular reactions and also to understand the internal arrangement of different molecules. X-ray diffraction studies and spectroscopy are also used in determining the structure of molecules.

Evidence from thermochemical data

For most reactions, an enthalpy change calculated using bond energies turns out to be extremely close to the observed enthalpy change during the reaction. However, this is not the case when we consider the enthalpy change during the hydrogenation of benzene. The theoretical enthalpy change for the hydrogenation of benzene is calculated using the enthalpy change for the hydrogenation of cyclohexene, and when hydrogen is added the enthalpy change is - 120 kJ mol^{-1}.

The Kekule model of benzene has three such double bonds. So it seems reasonable to suppose that when these three carbon-carbon double bonds are involve in a reaction with hydrogen the enthalpy change will be three times that of the hydrogenation of cyclohexene. Thus, the theoretical value of the enthalpy change for the hydrogenation of Kekule benzene would be - 360 kJ mol^{-1}.

When hydrogenation is carried out, the measured enthalpy change is only - 208 kJ mol^{-1}. This is **substantially less in magnitude** than the theoretical value and suggests that the addition reaction with hydrogen is not occurring across a normal double bond. This indicated the structure of benzene must be more stable than is proposed.

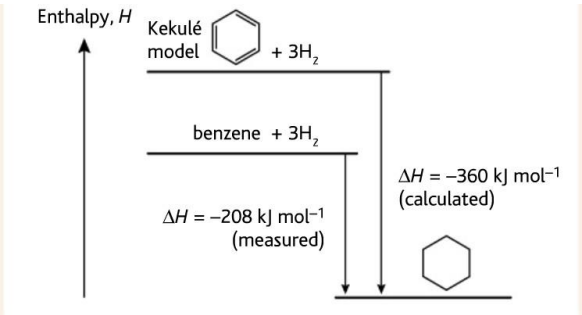
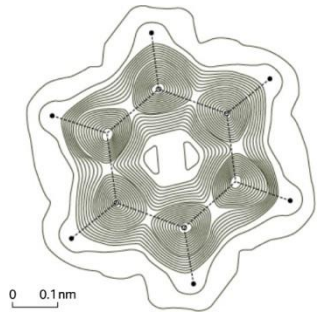


fig. 2.3.8 The difference between the calculated enthalpy change and the actual enthalpy change for the hydrogenation of benzene can be seen clearly. Data such as this made it imperative that a new model for the benzene model should be found.

Evidence from X-ray diffraction data and electron density maps



X-ray diffraction studies can be used to measure bond lengths. A carbon-carbon single bond in a cyclohexane ring has a bond length of 0.154 nm. A carbon-carbon double bond in a cyclohexene ring has a bond length of 0.133 nm. If the Kekule model of benzene structure held true, we would expect there to be two different bond lengths in the molecule – one for single bonds and one for the double bonds.

X-ray diffraction gives only a single value for the carbon-carbon bonds in the benzene ring.

The bond length is 0.139 nm and this suggests that all the bonds are the same in nature, and that the bond length is somewhere between that of a single and that of a double bond.

Evidence from infrared (IR) data

The infrared spectroscopic comparisons between cyclohexene and benzene also provide evidence for the unique structure of the benzene molecule.

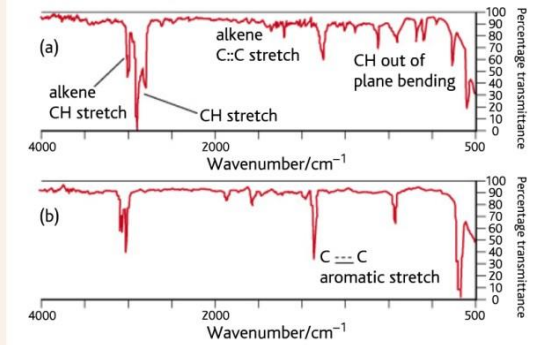


fig. 2.3.9 IR spectra for (a) cyclohexene and (b) benzene.

2 THE FINAL MODEL OF BENZENE

The arrangement of the electrons in benzene is very different. Each carbon atom forms a single sigma bond with each of the two carbon atoms joined to it. This forms the skeleton of the molecule, giving a planar hexagonal ring.

Each carbon atom has one p orbital containing a single electron, and it is the lobes of these p orbitals that fuse to form a single ring of charge above and another single ring below the sigma-bonded skeleton. Within these extended pi bonds, the electrons are free to move around the ring – they are localised. It is this delocalisation that causes all the carbon-carbon bonds in benzene to be identical, and which also makes the benzene molecule so unexpectedly stable.

3 NAMING ARENES

-Br	-bromo
-Cl	-chloro
-F	-fluoro
-OH	-hydroxy
=O	-oxo
$-NH_2$	-amino
$-NO_2$	-nitro
$-C_6H_5$ (Benzene ring)	-phenyl
$-CH_3$	-methyl
$-CH_2CH_3$	-ethyl
$-CH_2CH_2CH_3$	-propyl
$-CH_2CH_2CH_2CH_3$	-butyl

4 REACTIONS OF BENZENE

Combustion of benzene

All hydrocarbons burn in air or oxygen to produce carbon dioxide and water, providing there is sufficient oxygen available. The reaction for benzene is:

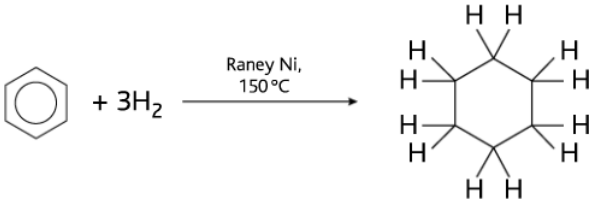
$$2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(l)$$

The complete combustion of benzene requires a large volume of oxygen. When benzene burns there may well be insufficient oxygen and some unburned carbon may remain – this will make the **flame yellow in colour and smoky**.

Addition reactions of benzene

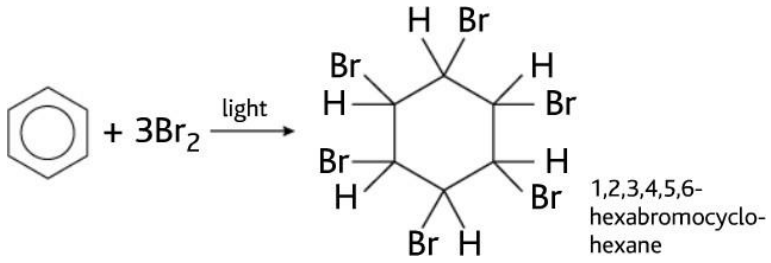
-With hydrogen

When benzene is mixed with hydrogen in the presence of a Raney nickel catalyst at a moderate temperature (150° C).



-With halogens

Benzene undergoes addition reactions with bromine rapidly in the presence of UV light or bright sunlight to form 1,2,3,4,5,6-hexabromocyclohexane.



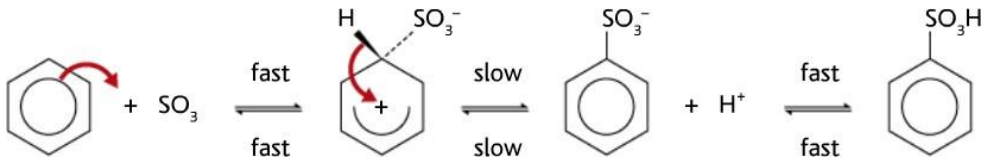
The rapidity of the reaction and the requirement for light to overcome the activation energy suggest a free-radical addition.

Substitution reactions of benzene

- **With fuming sulfuric acid (Sulfonation)**

Fuming sulfuric acid is concentrated sulfuric cid that contains additional sulfur trioxide, with which benzene reacts more readily because the sulfur trioxide is an effective electrophile.

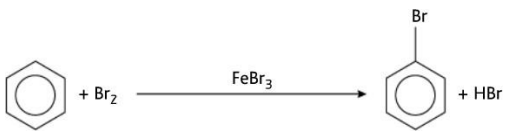
This very strong acid reacts under reflux with benzene to give benzenesulfonic acid, the electrophile being sulfur trioxide SO_3. Sulfonic acids contain the SO_3H group and are important commercially in the manufacture of detergents.



- With halogens

Benzene reacts very differently with halogens depending on whether the reaction takes place in the light or in the dark.

In dark, benzene does react with bromine unless there is a catalyst of iron(III) bromide or iron fillings are present – this catalyst is called a halogen carrier. The benzene, bromine and halogen carrier are refluxed together and bromobenzene is formed:



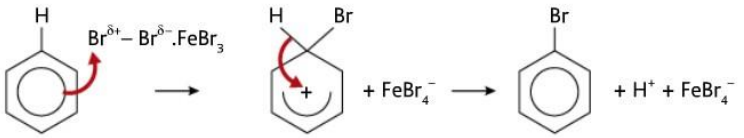
Iron can be used instead of iron(III) bromide because iron reacts with some of the bromine present to form iron(III) bromide:

$$2Fe(s) + 3Br_2(l) \rightarrow 2FeBr_3(s)$$

The iron(III) bromide polarises the bromine molecule, forming a complex:

$$Br\text{—}Br + FeBr_3 \rightarrow \overset{\delta+\quad\delta-}{Br\text{—}Br.FeBr_3}$$

This acts as an electrophile, forming first a weak π complex, and then the more stable σ complex:



A proton is then lost and this reacts to regenerate the iron(III) bromide, forming HBr:

$$H^+ + FeBr_4^- \rightarrow FeBr_3 + HBr$$

Nitration of benzene

Benzene does react with concentrated nitric acid, yet it does react with a mixture of concentrated nitric and concentrated sulfuric acid – this is called a nitrating mixture. The product is nitrobenzene, providing the temperature is kept low.

The round-bottomed reaction flask with the nitrating mixture is held in a beaker of cold water by a clamp. The reaction flask has a tap funnel containing benzene. The benzene is slowly added dropwise to the mixture in the flask. The acids react and give out heat, as does the addition of benzene to the nitrating mixture – this is why the cold water and slow addition are needed. **If temperature is too high, multiple substitutions occur**.

HSW The nitronium ion, NO_2^+

The first step of nitration involves the production of the NO_2^+ (nitronium) cation in the reaction of concentrated nitric acid and concentrated sulfuric acid:

$$HNO_3(l) + 2H_2SO_4(l) \rightleftharpoons NO_2^+(sol) + 2HSO_4^-(sol) + H_3O^+(sol)$$

The nitric acid acts as a base and accepts protons from the sulfuric acid. Evidence for the existence of this cation comes from being able to isolate salts – $NO_2^+ClO_4^-$ for example – and from spectroscopy.

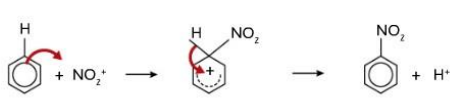


fig. 2.3.21 **The reaction mechanism for the nitration of benzene.**

Figure 2.3.21 shows the mechanism of the reaction. There is a ring of negative charge above and below the benzene ring (caused by the delocalised electrons in the extended π bonds) and this allows the nitronium ion to act as an electrophile, forming a weak complex using a pair of electrons from the ring.

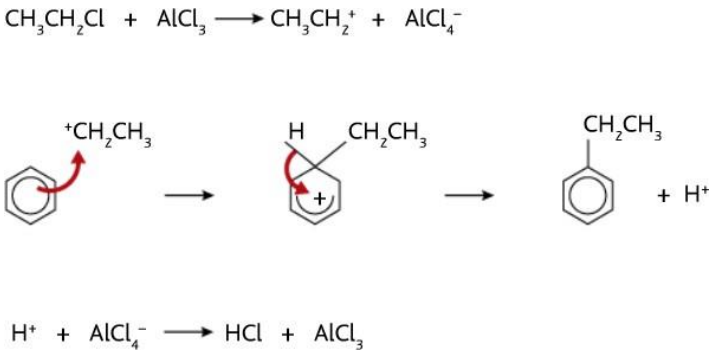
In the second stage of the reaction, this intermediate breaks down very rapidly by losing a proton to form the product.

Friedel-Crafts reactions

- Alkylation of benzene (with halogenoalkanes)

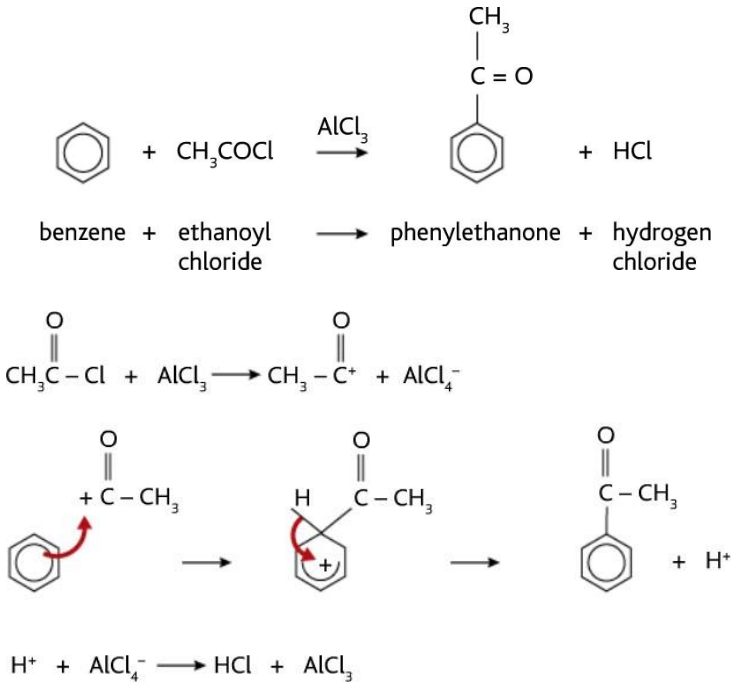
This reaction provides a means of substituting an alkyl group in a benzene ring. It involves refluxing benzene with a halogenoalkane in the presence of a halogen carrier catalyst, such as aluminium chloride:

The halogen carrier, aluminium chloride polarises the halogenoalkane molecule, promoting the formation of an electrophilic alkyl cation. This is attracted to the benzene complex, forming first a pi and then a sigma complex. This breaks down to form alkylbenzene product.



- Acylation of benzene (with acyl chlorides)

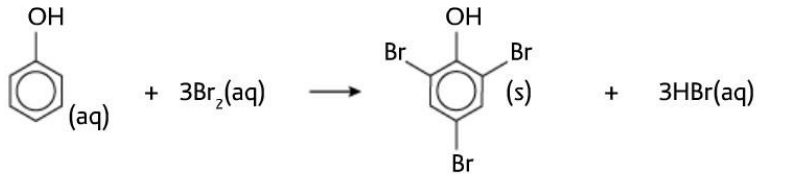
A reaction similar to alkylation takes place when benzene is refluxed with acyl chloride. The product is a ketone.



5 REACTIONS OF PHENOL

Reaction of phenol with bromine water

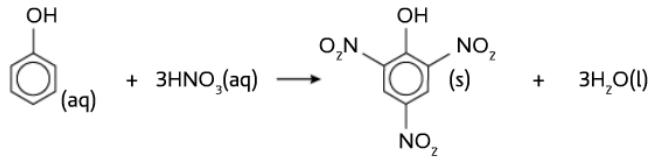
When bromine water is added to a solution of phenol in water, multi-electrophilic substitution takes place immediately, without heating or introducing a halogen carrier. The bromine water is decolurised. The product is a white precipitate of 2,4,6-tribromophenol, which smells of antiseptic.



phenol bromine solution 2,4,6-tribromophenol hydrogen bromide

Reaction of phenol with dilute nitric acid

When dilute nitric acid is added to a solution of phenol, a white precipitate of 2,4,6-trinitrophenol is formed. Again this is a multiple substitution reaction. Compared to benzene, phenol does not need sulfuric acid to assist nitration and the nitric acid is dilute. The substitution happen in the 2,4 and 6 positions of the ring.



phenol nitric acid 2,4,6-trinitrophenol water

2 Organic nitrogen compounds: amines, amides, amino acids and proteins

1 Amines

The amines are organic compounds based on ammonia, where one or more of the three hydrogen atoms have been substituted by an alkyl or aryl group. The number of these groups determines whether the compound is a primary amine, a secondary amine or a tertiary amine.

- If one hydrogen atom has been replaced, then it is a primary amine.
- If two hydrogen atoms have been replaced, then it is a secondary amine.
- If three hydrogen atoms have been replaced, then it is a tertiary amine.

2 The properties and reactions of primary amines

The physical and chemical properties of the simplest amines are similar to those of ammonia. So, methylamine and ethylamine are gases at room temperature and smell like ammonia. Propylamine and butylamine are liquids at room temperature. Like ammonia, alkyl amines with short hydrocarbon chains dissolve readily in water because they can hydrogen bond with it. Phenylamine, with its large non-polar benzene ring, is only slightly soluble in water. **Tertiary amines are also not soluble** because hydrogen bonding is not possible and the interactions between molecules are only van der Waals forces.

Amines as bases

Primary amines, like ammonia, can act as Bronsted-Lowry bases. The lone pair of electrons on the nitrogen atom of ammonia and amines is a proton acceptor.

$$K_b = [RNH_3^{\oplus}][OH^{\ominus}] / [RNH_2]$$

$$pK_b = -\log K_b$$

Reaction with water

Ammonia acts as a Bronsted-Lowry base and a small proportion of the dissolved molecules react with water to form a weakly alkaline solution.

- Butylamine

Butylamine and other amines act as Bronsted-Lowry bases in a similar manner by removing H^+ ions from water molecules to form an alkaline solution containing hydroxide ions.

$$C_4H_9NH_2\ (aq) + H_2O\ (aq) \rightleftharpoons C_4H_9NH_3^+(aq) + OH^-\ (aq)$$

As with ammonia, the reaction of amines with water is reversible so alkyl amines are also **weak bases, although stronger than ammonia**. This is because the alkyl group is electron releasing and increases the electron density on the lone pair on the nitrogen. This effect makes the lone pair more attractive to protons than the lone pair on the nitrogen in ammonia. The equilibrium lies further to the right than the equilibrium involving ammonia.

- Phenylamine

By contrast, phenylamine is a **much weaker base than ammonia** because **the lone pair in phenylamine is delocalised into the π cloud of the benzene ring** and is less attractive to protons than the lone pair in ammonia. Therefore, the equilibrium for the reaction of phenylamine with water lies further to the left than that for ammonia.

$$C_6H_5NH_2\ (l) + H_2O\ (l) \rightleftharpoons C_6H_5NH_3^+\ (aq) + OH^-\ (aq)$$

Formation of salts

Amines react even more readily than they do with water. The lone pair on the nitrogen atom rapidly accepts an H^+ ion from the acid to form a substituted ammonium salt.

- Ethylamine

When the vapour of gaseous amines such as ethylamine reacts with hydrogen chloride gas, the product, ethylammonium chloride, forms as a white smoke. The smoke settles as a white solid.

$$CH_3CH_2NH_2\ (g) + HCl\ (g) \rightarrow CH_3CH_2NH_3^+Cl^-$$

This reaction is very similar to that of ammonia with hydrogen chloride to form ammonium chloride.

- Phenylamine

Phenylamine, $C_6H_5NH_2$, is only slightly soluble in water, but it dissolves in concentrated hydrochloric acid very easily. This is because it reacts with H^+ ions in the acid to form phenylammonium ions which are soluble in the aqueous mixture.

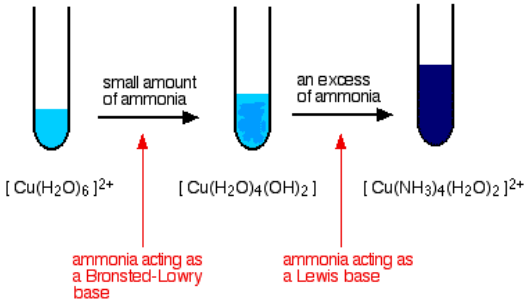
$$C_6H_5NH_2\ (l) + H^+\ (aq) \rightarrow C_6H_5NH_3^+\ (aq)$$

If a strong base, such as sodium hydroxide, is added to the aqueous phenylammonium ions, H^+ ions are removed from the phenylammonium ions and yellow, oily phenylamine reforms.

$$C_6H_5NH_3^+ (aq) + OH^- (aq) \rightarrow C_6H_5NH_2 (l) + H_2O (l)$$

Amines as ligands

When ammonia and amines act as bases and accept a proton, they do so by donating a lone pair of electrons to the proton. Ammonia and amines can also donate a lone pair of electrons to transition metal ions and act as ligands.


small amount of ammonia
an excess of ammonia
[Cu(H2O)6]2+
[Cu(H2O)4(OH)2]
[Cu(NH3)4(H2O)2]2+
ammonia acting as a Bronsted-Lowry base
ammonia acting as a Lewis base

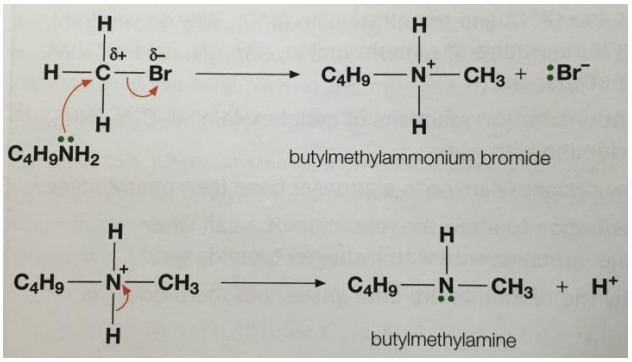
When butylamine is added to aqueous copper(II) sulfate solution, a deep blue solution is formed. Four butylamine molecules replace four water ligands and a deep blue complex is formed.

$$4C_4H_9NH_2 (aq) + [Cu(H_2O)_6]^{2+} (aq) \rightarrow [Cu(C_4H_9NH_2)_4(H_2O)_2]^{2+} (aq) + 4H_2O (l)$$

Amines as nucleophiles

- Reaction with halogenoalkanes

Amines are nucleophiles as well as bases and ligands, just like ammonia. As nucleophiles, their lone pair of electrons is attracted to any positive ion or positive centre in a molecule. So, amines react with the δ^+ carbon atoms in the C-Hal bond of halogenoalkanes in a nucleophilic substitution reaction. The protonated amine formed in the first step then loses a proton to form a secondary amine.



As with the reaction of ammonia with halogenoalkanes **further reaction is possible**. The lone pair on the nitrogen atom of the secondary amine product is more reactive than the lone pair on the primary amine reagent because of the inductive effect of the extra alkyl group.
So the secondary amine can also react with the halogenoalkane in a reaction which forms a tertiary amine.

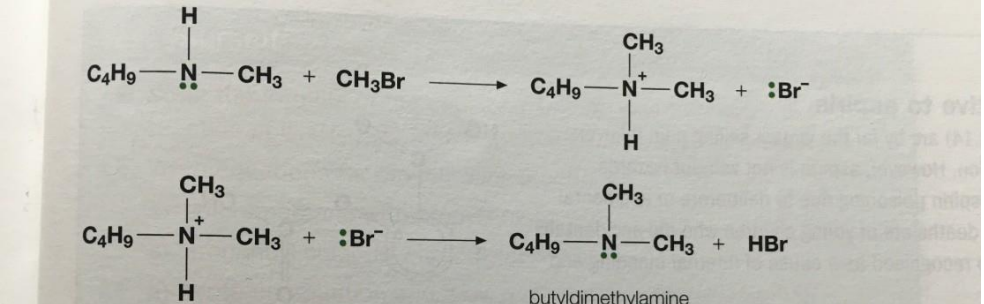
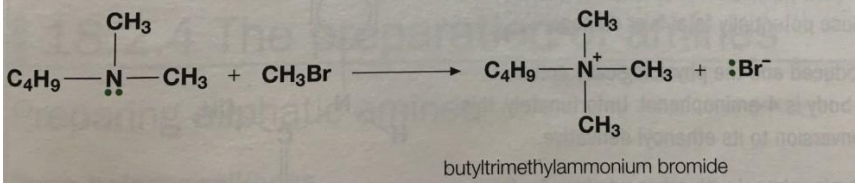


Figure 18.2.11 Formation of the tertiary amine butyldimethylamine.

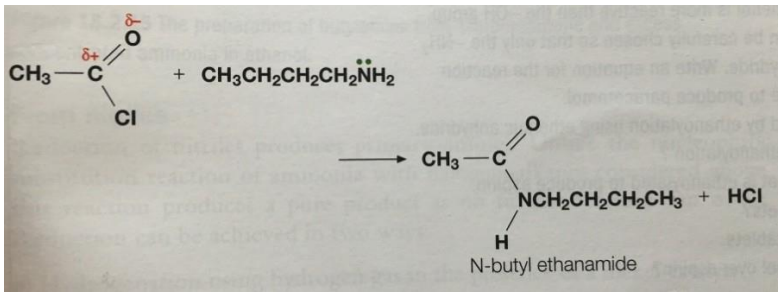
The tertiary amine similarly can react further to form a **quaternary ammonium salt** (Figure 18.2.12).



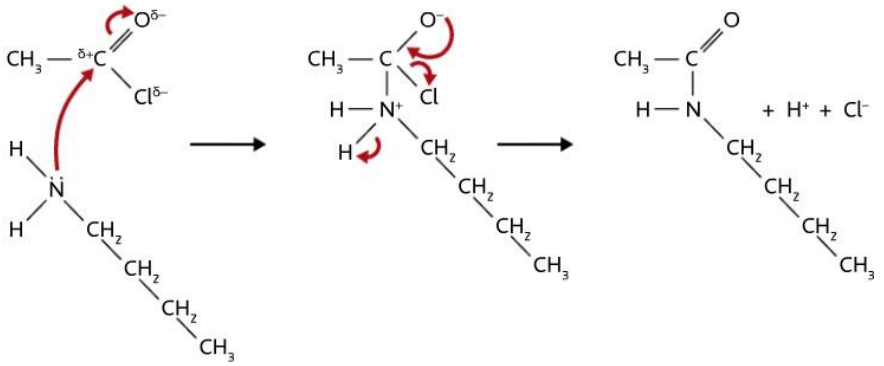
It is possible to limit further reaction by using an excess of the primary amine so that there is a much greater chance of the primary amine rather than the secondary amine acting as nucleophile with the halogenoalkane molecules.

- Reaction with acyl chlorides

Amines also react as nucleophiles with the δ^+ carbon atoms in the COCl group of acyl chlorides such as ethanoyl chloride. The reaction forms an N-substituted amide. A reaction of this type is involved in the manufacture of paracetamol.



The amine, with a lone pair of electrons on the nitrogen atom, acts as a **nucleophile** and attacks the positive centre in the ethanoyl chloride molecule (fig. 2.4.9). This positive centre is caused by withdrawal of electrons in the C=O bond because of the greater electronegativity of the oxygen atom – this is further enhanced by the electronegative chlorine atom. The nitrogen atom attacks the carbon atom and this is accompanied by the loss of a chlorine and a proton.

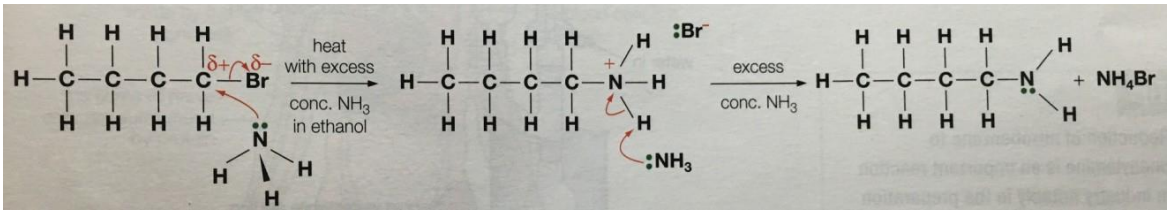


3 THE PREPARATION OF AMINES

Preparing aliphatic amines

- From halogenoalkanes

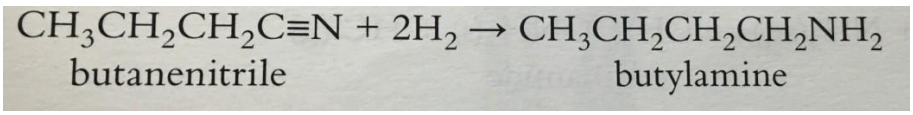
Aliphatic amines can be prepared by heating the corresponding halogenoalkanes in a sealed flask with excess ammonia in ethanol. During the first step of the reaction ammonia acts as a nucleophile and then in the second step it acts as a base to remove a proton from the salt initially formed.



- From nitriles

Reduction of nitriles produces primary amines. Unlike the nucleophilic substitution reaction of ammonia with halogenoalkanes, this reaction produces a pure product as no further reaction can occur. Reduction can be achieved in two ways:

a) Hydrogenation using hydrogen gas in the presence of a nickel catalyst.



b) Reduction using $LiAlH_4$ in ethoxyethane, followed by dilute acid.

$$CH_3CH_2CH_2C{\equiv}N + 4[H] \rightarrow CH_3CH_2CH_2CH_2NH_2$$

Preparing aromatic amines

Benzene and other aromatic compounds can be nitrated to form a nitro-compounds using a mixture of concentrated nitric acid and concentrated sulfuric acid. These nitro-compounds can produce aromatic amines.

Production of phenylamine

Phenylamine can be produced by reduction of nitrobenzene using a mixture of tin and concentrated hydrochloric acid:

Tin reacts with concentrated hydrochloric acid to produce tin(II) ions and hydrogen:

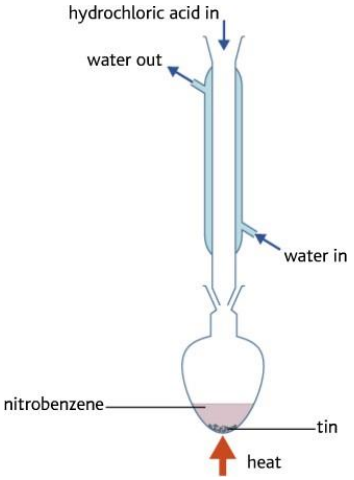
$$Sn(s) + 2HCl(aq) \rightarrow Sn^{2+}(aq) + 2Cl^{-}(aq) + H_2(g)$$

The tin(II) ions are oxidised to tin(IV) ions and these reduce the $-NO_2$ group to the $-NH_2$ group:

$$Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^{-}$$

$$C_6H_5NO_2(l) + 6H^{+}(aq) + 6e^{-} \rightarrow C_6H_5NH_2(l) + 2H_2O(l)$$

The flask is then cooled and sodium hydroxide solution is added to redissolve the initial precipitate of tin(IV) hydroxide, $Sn(OH)_4$ – tin(VI) hydroxide is amphoteric and with excess alkali produces the soluble $Sn(OH)_6^{2-}$ ion.



Water is then added and steam distillation is used to separate the mixture of phenylamine and water. The distillate initially collected is cloudy because it is an emulsion of phenylamine and water. When the distillate is clear, only water is distilling over.

Powdered sodium chloride is added to the distillate and the mixture is transferred to a separating funnel. This is shaken well – phenylamine is significantly soluble in water, but very much less so in saturated sodium chloride solution. This process is called salting out.

The mixture is then transferred to a separating funnel and ethoxyethane is added and shaken, relieving the pressure in the separating funnel occasionally by opening the tap. The layers are allowed to separate, and then lower aqueous layer is run off into a small beaker.

The ethoxyethane layer is transferred to a small conical flask, and further extraction of the aqueous layer with further portions of ethoxyethane is carried out. The ethoxyethane extracts are combined – this is an example of solvent extraction.

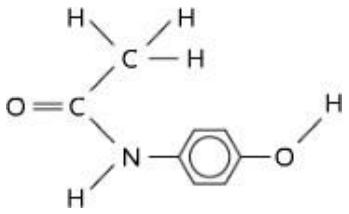
Pellets of potassium hydroxide are added to dry the ethoxyethane extract. Potassium hydroxide is better than calcium chloride or anhydrous sodium sulfate because, being alkaline, it will remove any traces of hydrochloric acid.

The ethoxyethane is distilled off and finally phenylamine is distilled off, collecting the fraction between 180 and 185°C.

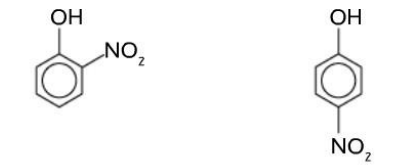
4 MAKING PARACETAMOL

Paracetamol is a widely used painkiller in the world. It can be made in a stepwise procedure using phenol as a starting material.

Paracetamol molecule:



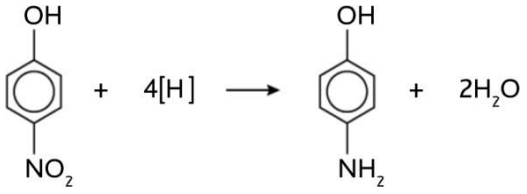
Step 1: Phenol is nitrated using sulfuric acid and sodium nitrate. Unlike the nitration of benzene, it is not necessary to use a mixture of concentrated sulfuric and nitric acids because the ring is activated by the -OH group. A mixture of two isomers is produced.



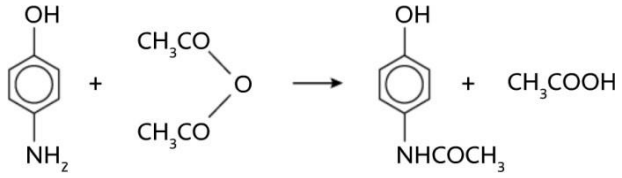
2-nitrophenol 4-nitrophenol

Step 2: The two isomers are separated by fractional distillation. 4-nitrophenol has a higher melting point than 2-nitrophenol because more effective hydrogen bonding occurs between molecules in 4-nitrophenol.

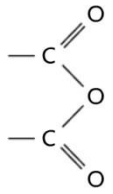
Step 3: The 4-nitrophenol is reduced to 4-aminophenol using a reducing agent such as sodium tetrahydridoborate(III) in an alkaline medium:



Step 4: The 4-aminophenol is reacted with ethanoic anhydride to give paracetamol:



The CO.O.CO arrangement should look like this:



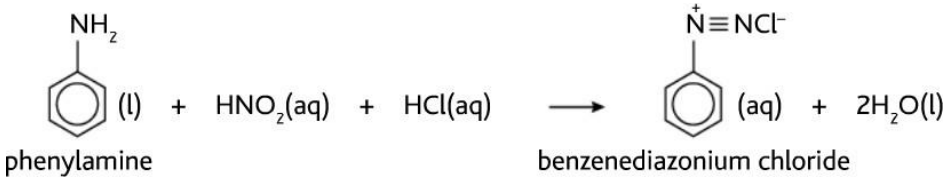
Many processes used for the synthesis of drugs involve molecules with chiral centres. This leads to the need to consider the stereochemistry of the products at each stage. There is no chiral centre in paracetamol, or any intermediates, which makes this manufacturing process much simpler.

5 MAKING AZO DYES

Aromatic amines, such as phenylamine, can be converted into diazonium salts by reaction with nitrous acid HNO_2. Nitrous acid is a very unstable compound which exists only in aqueous solution and decomposes at room temperature. The nitrous acid must be prepared as needed in situ by mixing ice-cold solutions of sodium nitrate and dilute hydrochloric acid:

$$NaNO_2(aq) + HCl(aq) \rightarrow NaCl(aq) + HNO_2(aq)$$

Nitrous acid is reacted with phenylamine at a temperature of less than 5°C.



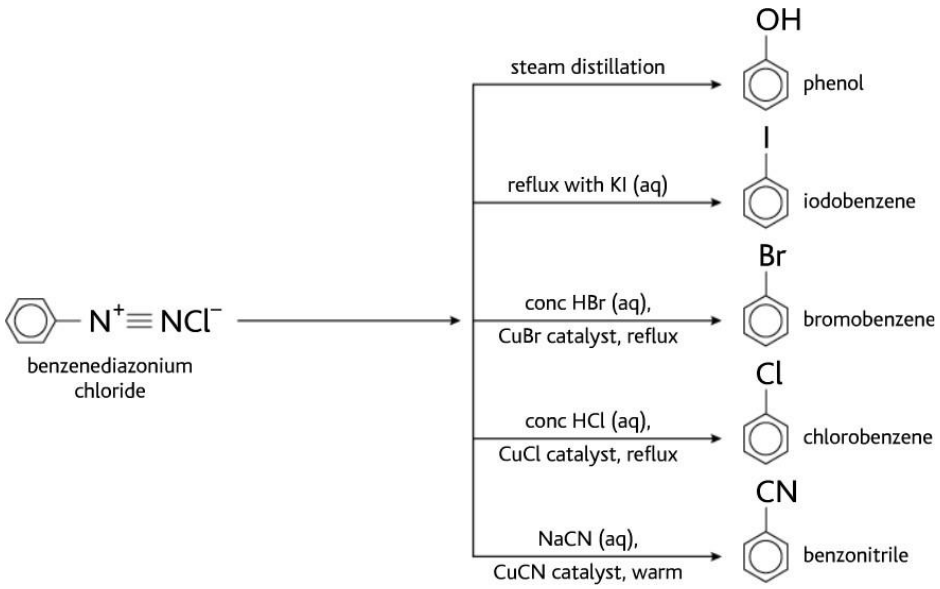
Diazonium compounds are generally very unstable at room temperature. If aliphatic amines are used, diazonium salts are not produced because they are so unstable – they decompose almost immediately as they are formed, even at a very low temperature. Aromatic diazonium salts, such as benzenediazonium chloride, are more stable, at least up to 10°C or so. This additional stability results from the delocalised electrons of the benzene ring.

The high activity of diazonium salts can be put to use in a wide variety of situations in organic synthesis procedures. The use of diazonium ions is based on two aspects of their chemistry – attack of the diazonium benzene ring by nucleophiles, and the ability of diazonium salts to couple with other molecules. When nucleophiles react with the benzene

ring, nitrogen gas is evolved – this does not happen when diazonium ions couple with other molecules.

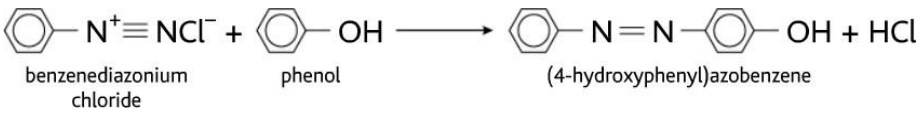
Diazonium compound reactions with nucleophiles

The diazonium group opens the benzene ring to attack by nucleophiles, such as amines. **Nitrogen gas is evolved in these reactions**.



Diazonium compound reactions as electrophiles

The benzenediazonium ion caries a positive charge and so is a strong electrophile. It reacts readily in cold alkaline solution both with aromatic amines an with phenols – they attack giving brightly coloured diazo-compounds. These reactions, joining two aromatic rings together, are known as coupling reactions. In coupling reactions, no nitrogen gas is produced.



The diazo-compounds produced are complex molecules with a minimum of two aromatic rings joined by an $N \equiv N$ coupling. Unlike the diazonium compounds from which they are made, di-azo compounds are extremely stable and unreactive. The bright colours they have are the result of the extensive delocalised electron systems that spread across the entire molecule through the $N \equiv N$ coupling.

The aromatic rings are joined together through the azo group (– N = N –). These dyes cam absorb light in the visible part of the spectrum.

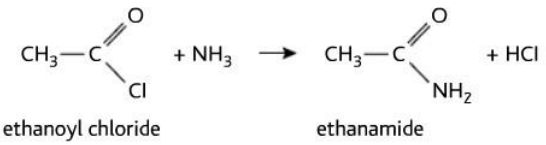
6 AMIDES

The general formula for the amides is $RCONH_2$, where R is an alkyl group. Amides are carboxylic acid derivatives.

Preparing amides

Reaction with concentrated ammonia

Acyl chlorides react with concentrated ammonia to produce amides. These reactions take place on mixing the reactants and without heating.



ethanoyl chloride ethanamide

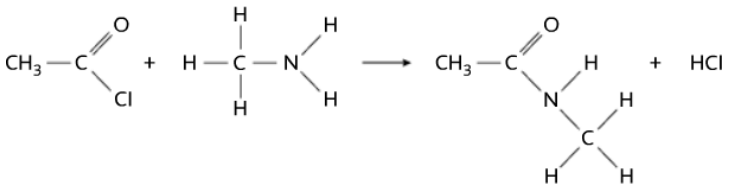
fig. 1.6.75 Reaction of acyl chlorides with ammonia.

Because of the acid/base nature of the products, a further reaction takes place:

$$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$$

Reaction with amines

A similar reaction occurs between acyl chlorides and amines to produce a substituted amide.



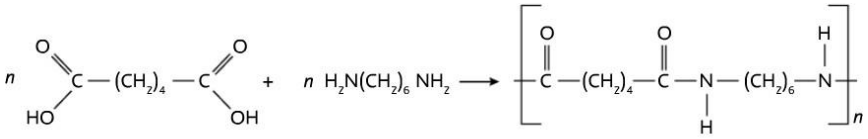
methylamine *N*-methylethanamide

In naming compounds such as this, N-methyl means that a methyl group is attached to the nitrogen atom of the amide.

7 POLYAMIDES

Polyamides are polymers with amide links between monomer units.

1-) Condensation polymerisation



hexanedioic acid 1, 6-diaminohexane nylon 6,6

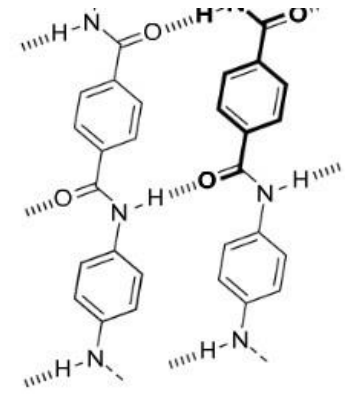


fig. 2.4.20 The structure of Kevlar: it consists of long polymer chains of paraphenylene terephthalamide – sometimes called para-aramid fibres – with strong hydrogen bonds between the chains.

2-) Addition polymerisation

Poly(propenamide)

This is an addition polymer – although the 'amide' in the name might suggest that it is a condensation polymer. It is formed by polymerising 2-propenamide (sometimes called acrylamide):

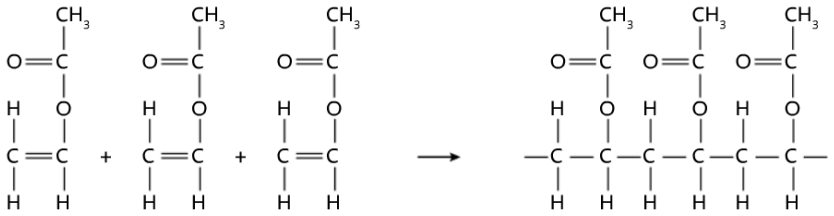
2-propenamide poly(propenamide)

The polymer chains in poly(propenamide) can be readily cross-linked with other chains. The resulting polymer with cross-chains produces a gel which has a huge capacity to absorb water. It can be used for making soft contact lenses. In the non-cross-linked form it is used as a thickener and a filler in facial surgery.

Poly(ethenol)

Poly(ethenol) is an addition polymer – it is sometimes called poly(vinyl alcohol).

It is not manufactured in the usual way by polymerising a monomer, but from another polymer by the process of ester exchange. In the first stage of manufacture, ethenyl ethanoate is polymerised to form poly(ethenyl ethanoate):



ethenyl ethanoate poly(ethenyl ethanoate)

The new polymer is then reacted with methanol to give poly(ethenol) and methyl ethanoate. The extent of ester exchange can be controlled simply by altering the temperature:

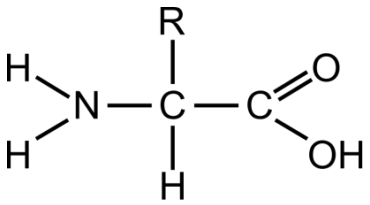
poly(ethenyl ethanoate) poly(ethenol)

The solubility of the final polymer depends on the percentage of ester groups that have been replaced – it ranges from effectively insoluble, through soluble in hot/warm water, to soluble in cold water.

Poly(ethenol) is used to make the liquid detergent capsules and soluble laundry bags.

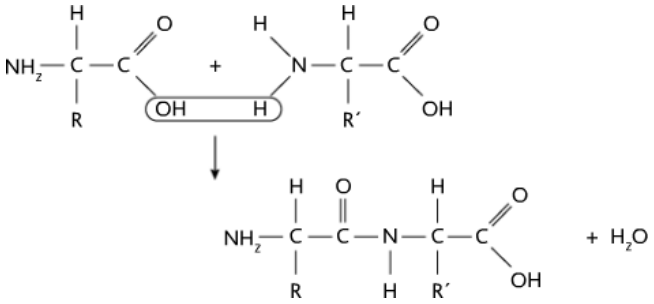
8 AMINO ACIDS AND PROTEINS

Amino acids are organic compounds containing an amide and a carboxylic acid group. They have the general formula:



The peptide group

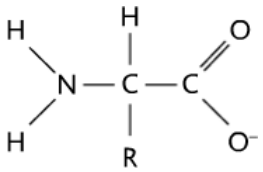
When two amino acids join together, they undergo a condensation reaction and lose a molecule of water. The resulting bond is a peptide bond and the molecule is called a dipeptide.



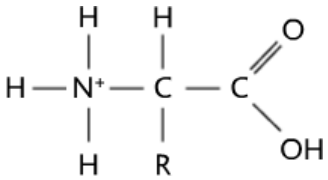
Chains of many peptide groups form polypeptides which fold to form the proteins.

Acidic and basic properties of amino acids

Amino acids have interesting properties because they contain both an acidic group and a basic group. In an alkaline solution, the amino acid loses a proton and forms a negative ion:

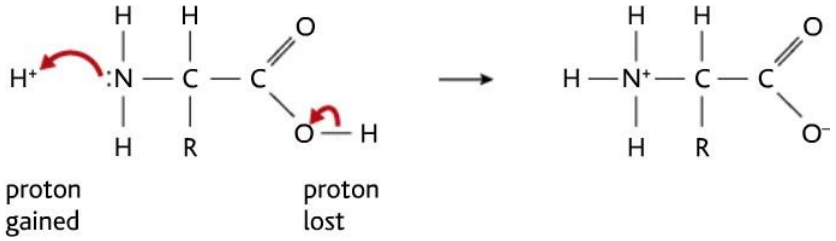


In an acidic solution, the molecule receives a proton and forms a positive ion:



In a neutral solution, amino acids exist with both the positive and negative ions within the same molecule. This species is called a zwitterion.

Amino acids can exist as zwitterions when in the solid state. This explains their relatively high melting temperature when compared with similar compounds and why they dissolve in water. Amino acids do not dissolve in organic solvents.

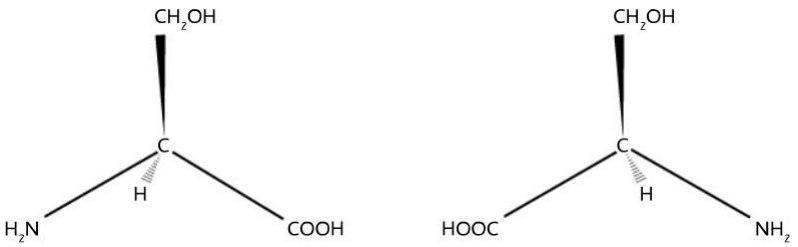


Identifying amino acids

Mixtures of amino acids can be separated and identified using chromatography. Comparing the position of spots on a chromatogram of the mixture with known reference amino acids allows the identification to be made. Amino acid spots in a chromatogram are colourless, so to be viewed they must be stained by spraying them with ninhydrin. This produces coloured spots.

Optical isomerism in amino acids

All amino acid molecules have a chiral centre and show optical isomerism. Chiral molecules rotate the plane of polarisation of monochromatic plane-polarised light. The extent of rotation is equal but opposite for two optical isomers.



Colours in A2 Chemistry

Colour of transition metal ions

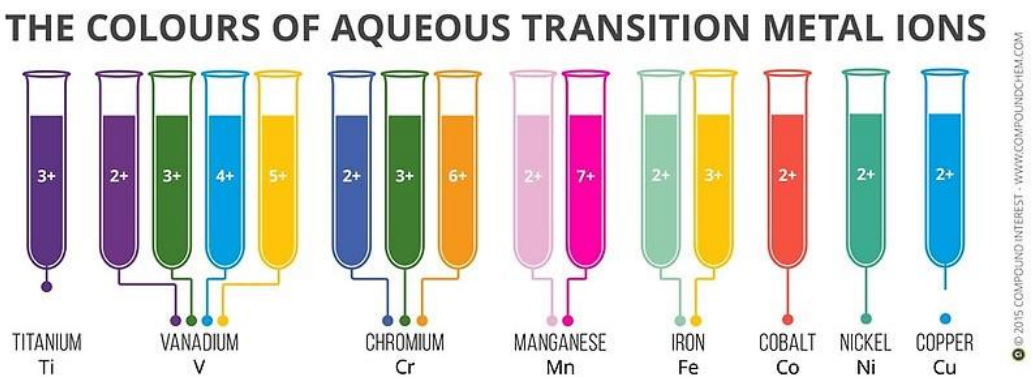
Oxidation number	+1	+2	+3	+ 4	+5	+6	+7
Colour of Sc			Colourless	-	-	-	-
Colour of Ti	-		Violet	Colourless	-	-	-
Colour of V		Purple	Green	Blue	Yellow	-	-
Colour of Cr		Pale blue	Green			Orange	-
Colour of Mn		Pale pink	Violet				Dark purple
Colour of Fe		Pale green	Brown		-		-
Colour of Co		Pink				-	-
Colour of Ni		Green			-	-	-
Colour of Cu	Colourless	Blue	-	-	-	-	-
Colour of Zn		Colourless	-	-	-	-	-

The most common oxidation number of most of the elements is +2, due to the loss of the outer two 4s electrons. However, the underlying d orbitals are very close to the 4s level, and so it is relatively easy to lose electrons from these as well.

Most of the transition metals form compounds which dissolve in water to form coloured solutions. Changes in the colour of solutions can alert us to a change in oxidation number of the ion. Where the ion has a $3d^0$ or $3d^{10}$ arrangement, the solution of the ion is colourless.

Transition metals usually show their highest oxidation numbers when they are combined with oxygen or fluorine, the most electronegative element. The highest oxidation numbers of all the elements up to and including manganese correspond to the involvement in bonding of all of the electrons outside the argon core. Beyond manganese the 3d electrons are held more strongly because of the increasing nuclear charge and so, by and large, the common oxidation numbers involve the 4s sub-shell only.

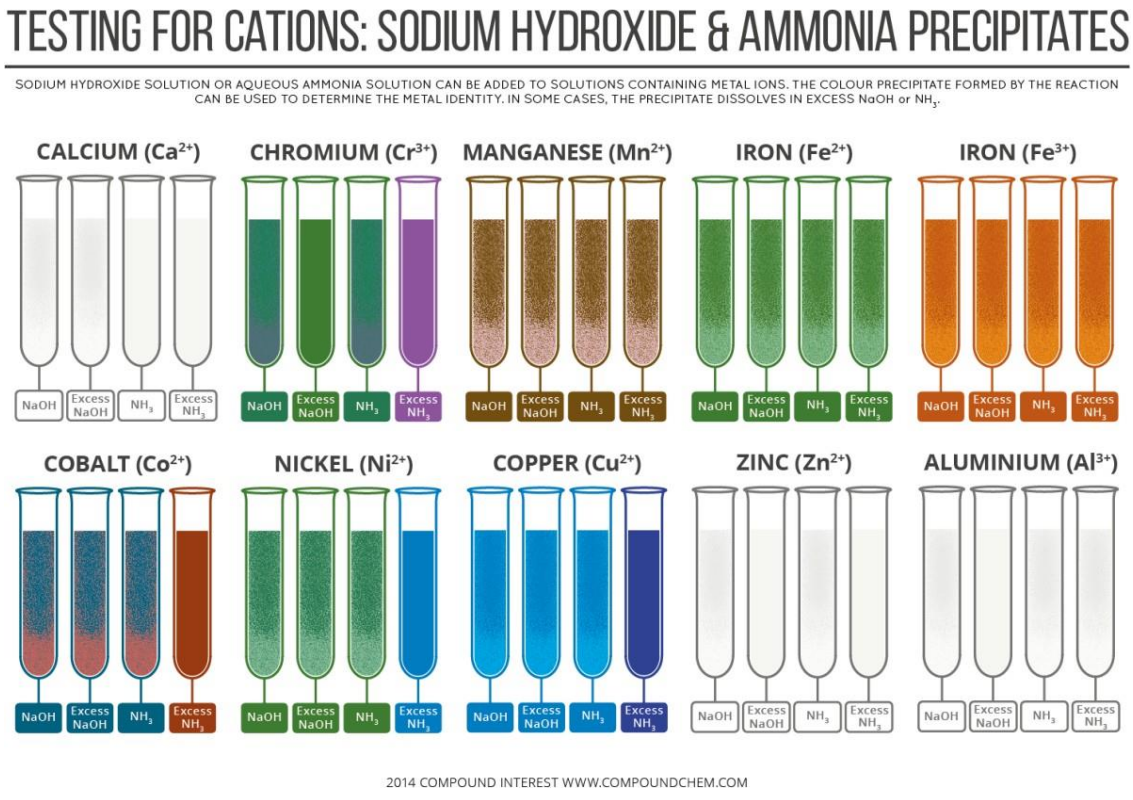
When the elements exhibit very high oxidation numbers, they do not form simple ions. Either they are involved in covalent bonding or they form polyatomic ions.



Testing for metal ions

Aqua ion	NaOH (aq)	Excess NaOH (aq)	NH_3 (aq)	Excess NH_3 (aq)
Cr^{3+}	Green ppt: $Cr(H_2O)_3(OH)_3$	Green solution: $[Cr(H_2O)_2(OH)_4]^-$	Green ppt: $Cr(H_2O)_3(OH)_3$	Yellow solution: $[Cr(NH_3)_6]^{3+}$
Mn^{2+}	Cream-brown ppt: $Mn(OH)_2$	Insoluble	Cream-brown ppt: $Mn(OH)_2$	Insoluble
Fe^{2+}	Dark green ppt: $Fe(OH)_2$	Insoluble	Dark green ppt: $Fe(OH)_2$	Insoluble
Fe^{3+}	Rusty red ppt: $Fe(H_2O)_3(OH)_3$	Insoluble	Rusty red ppt: $Fe(H_2O)_3(OH)_3$	Insoluble
Ni^{2+}	Green ppt: $Ni(OH)_2$	Insoluble	Green ppt: $Ni(OH)_2$	Blue solution: $[Ni(NH_3)_6]^{2+}$
Cu^{2+}	Blue ppt: $Cu(OH)_2$	Insoluble	Blue ppt: $Cu(OH)_2$	Deep blue solution: $[Cu(NH_3)_4(H_2O)_2]^{2+}$
Zn^{2+}	White ppt: $Zn(OH)_2$	Colourless solution	White ppt: $Zn(OH)_2$	Colourless solution

*$Mn(OH)_2$ and $Fe(OH)_2$ are white precipitates, yet they both turn brown on standing on air.


TESTING FOR CATIONS: SODIUM HYDROXIDE & AMMONIA PRECIPITATES
SODIUM HYDROXIDE SOLUTION OR AQUEOUS AMMONIA SOLUTION CAN BE ADDED TO SOLUTIONS CONTAINING METAL IONS. THE COLOUR PRECIPITATE FORMED BY THE REACTION CAN BE USED TO DETERMINE THE METAL IDENTITY. IN SOME CASES, THE PRECIPITATE DISSOLVES IN EXCESS NaOH or NH3.
CALCIUM (Ca2+)
CHROMIUM (Cr3+)
MANGANESE (Mn2+)
IRON (Fe2+)
IRON (Fe3+)
COBALT (Co2+)
NICKEL (Ni2+)
COPPER (Cu2+)
ZINC (Zn2+)
ALUMINIUM (Al3+)
NaOH
Excess NaOH
NH3
Excess NH3
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Ligand exchange reactions for copper complexes

It is possible for one type of ligand to be replaced by another type.
Ligand exchange reactions often have a colour change associated with them.

Thiocyanate ions can replace one of the water ligands in $[Fe(H_2O)_6]^{3+}$.

$$[Fe(H_2O)_6]^{3+} + SCN^- \rightarrow [Fe(H_2O)_5SCN]^{2+} + H_2O$$

An aqueous Copper(II) sulphate solution is blue in colour because of the presence of $[Cu(H_2O)_6]^{2}$ ions. When concentrated hydrochloric acid is added to this solution the colour changes from blue to green. This happens because the $[CuCl_4]^{2-}$ ion is produced. The Cl^- ions have replaced the H_2O molecules in a ligand exchange.

$$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CuCl_4]^{2-} + 6H_2O$$

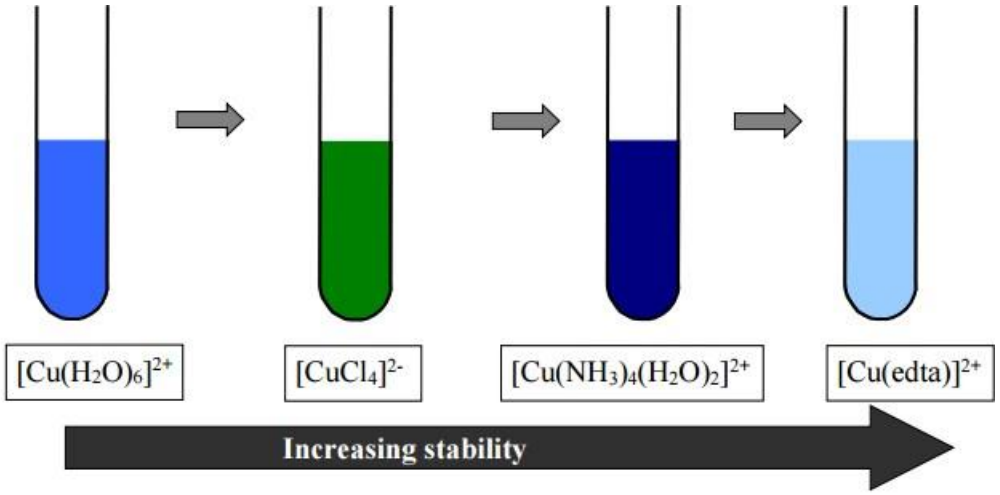
When ammonia is added a further change from green to deep blue takes place as ammonia molecules replace the chloride ions.

$$[CuCl_4]^{2-} + 4NH_3 + 2H_2O \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4Cl^-$$

If EDTA is then added yet another ligand exchange takes place and the solution turns pale blue.

$$[Cu(NH_3)_4(H_2O)_2]^{2+} + edta \rightarrow [Cu(edta)]^{2+} + 4NH_3 + 2H_2O$$

These changes take place because the complexes become more stable.



The stability of the $[Cu(edta)]^{2+}$ complex can be understood in terms of entropy.
As the one edta molecule replaces the six smaller ligands, the small ligands are released into solution and therefore have greater freedom of movement, so greater disorder and consequently the entropy increases.

Colour of chromium ions

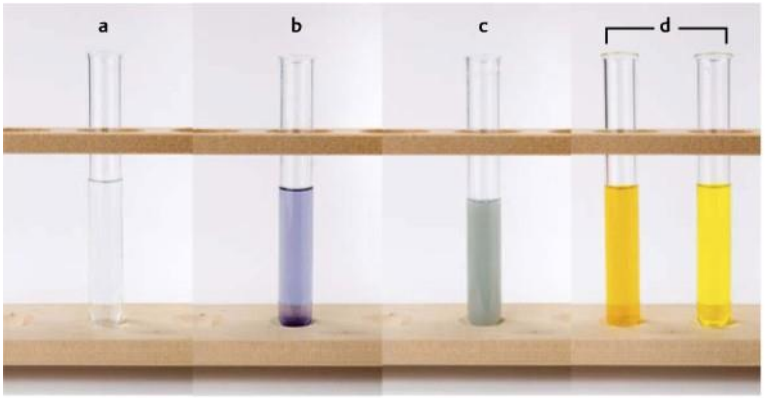


fig. 2.2.17 Chromium compounds produce many brightly coloured solutions.

a When chromium metal is dissolved in a dilute, oxygen-free, non-oxidising acid the pale blue colour of the Cr^{2+} ion is seen.

b The violet colour of this solution of chrome alum $[K_2SO_4{\cdot}Cr(SO_4)_3{\cdot}2H_2O]$ is typical of the $Cr(H_2O)_6^{3+}$ ion.

c The addition of an alkali to a solution in (b) gives a green solution containing $Cr(H_2O)_2(OH)_4^-$ ions.

d The dichromate ion ($Cr_2O_7^{2-}$), which predominates in acidic solution, has a reddish-orange colour; the chromate ion (CrO_4^{2-}) formed in alkaline solutions has a bright yellow colour.

Colour changes in important A2 chemistry reactions

Reaction			Observation
Aldehyde	+	Brady's reagent	Yellow/orange/red ppt
		Acidified potassium dichromate(VI)	Orange to green
		Fehling's or Benedict's solution	Blue to red
		Tollens' reagent	Silver mirror formed
Ketone	+	Brady's reagent	Yellow/orange/red ppt
Iodoform reaction (Positive result)			Yellow precipitate
Titration of potassium manganate(VII) with iron(II) ions:			Purple to pale pink
Titration of sodium thiosulfate and iodine solutions: ■ With starch near end-point			Brown to colourless Light brown colour → Black

Reaction of iodine with propanone

Iodine and propanone react, in the presence of acid, in a substitution reaction to form iodopropane. The reaction can be represented by:

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_2ICOCH_3(aq) + H^+(aq) + I^-(aq)$$

Brown → Colourless

Kinetic experiments can be carried out using different concentrations of propanone, iodine and hydrogen ions.

Using colorimeter

A colorimeter measures the absorption of light during the progress of the experiment. First, the colorimeter has to be calibrated using standard iodine solutions. The reaction mixture containing iodine will be light brown in colour and as the reaction proceeds the solution becomes paler and more light is transmitted.

By titration

During the experiment small aliquots of the reaction mixture are removed with a pipette. The withdrawn sample is put in a flask and excess sodium hydrogencarbonate is added. This effectively stops the reaction so no further change in iodine occurs during titration. The aliquots are titrated with standard solution of sodium thiosulfate using starch indicator near end-point. The measured values for the $[I_2]$ can be used to calculate the concentrations of the other substances involved.

$$\text{rate} = k[CH_3COCH_3][H^+]$$

The reaction is first order with respect to propanone and hydrogen ions, but zero order with respect to iodine. The overall order of reaction is two. The reaction involves various steps and the rate-determining step does not involve iodine. Hydrogen ions act as a catalyst – they are regenerated during the reaction.